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# ABSORPTION AND EMISSION SPECTRA OF NEODYMIUM AND ERBIUM COMPOUNDS

By JOHN AUGUSTUS ANDERSON

## INTRODUCTION

Of the eighteen or twenty elements belonging to the group of rare earths, seven or eight are of special interest to spectroscopists on account of their absorption phenomena. These are neodymium, praseodymium, erbium, holmium, samarium, dysprosium, thulium, and europium. The absorption spectra of solutions of these are remarkable on account of the number and relatively small width of the bands they present, some of which, notably the one near λ 4270, in the aqueous solution of some of the salts of neodymium, may very reasonably be spoken of as lines. These spectra have been the subject of a great number of investigations, a good summary of which may be found in the third volume of Kayser's *Handbuch der Spectroscopie*. In general it may be stated that the solutions of different salts of the same element show very similar absorption spectra, especially when conditions as to concentration and thickness of solution are the same.

The absorption spectra of the crystallized salts of some of these elements have been studied by a number of investigators, the most important work having been done on the crystals of various "didymium" salts by Henri Becquerel.[1] He found that the absorption of

[1] *C. R.*, **104**, 1691–1693, 1887; *Ann. Chim. et Phys.* (6), **14**, 257–279, 1888.

any given crystal depends, to some extent, upon the direction in which the light traverses it, the variation being, however, one of intensity and not of position of the bands. The crystals of different salts, as a rule, show different spectra, in speaking of which he says: "In passing from one spectrum to another, it may be seen, for example, that a given band is displaced, while neighboring bands are not; sometimes a series of bands moves as a whole, while other series are unaffected, . . . . finally, some bands, present in one case, may be entirely absent in another." He seems to find in this evidence in favor of the view held by many chemists, that "didymium," or its components, neodymium and praseodymium, are in reality a complicated mixture of several substances, for after comparing the spectra of the crystals with those of their corresponding solutions he says: "In general it may be stated that the spectra of all solutions differ very little from each other, while those of the crystals are quite different. It seems, then, that the matter forming didymium, when in solution is brought into the same condition, and that the presence of different acids in this condition has little or no influence on the absorption."[1] Becquerel also observed that, in case of the dry salts of "didymium," absorption spectra could be observed in white light diffusely reflected from them. The spectra thus observed he found to behave in a way very similar to those observed in crystals.

When the oxides or phosphates of some of these elements, notably erbium and neodymium, are heated to incandescence in a non-luminous flame such as that of a Bunsen burner, the spectrum emitted is not continuous, as in case of most solids and liquids, but consists of some bright bands superposed upon a comparatively faint continuous background. This was first observed in 1866 by Bahr and Bunsen[2] for the oxide and phosphate of erbium, since which time it has been found that the oxides of neodymium, holmium, and perhaps other elements show similar emission spectra, although they are not as brilliant as that of erbium. Bahr and Bunsen concluded that the emission of the oxide and phosphate of erbium is the same, noting, however, that the bands are more intense with the phosphate. They further concluded that the positions and relative intensities of the

[1] *Ann. Chim. et Phys.* (6), **14**, pp. 257 ff.

[2] *Liebigs Ann.*, **137**, 1–33, 1866.

bands agree with those of the absorption bands seen in the solutions of erbium salts. Thalén[1] in 1880 came to the same conclusion in regard to the agreement between the bands in the absorption and emission spectra of erbium. Lecoq de Boisbaudran[2] investigated the emission as well as the absorption of both erbium and neodymium, and found that the emission of erbium phosphate differs considerably from that of its oxide. That this difference was not due to impurities was evident from the fact that both the compounds were made from the same preparation, namely from a solution of erbium nitrate. He also compared them with the absorption spectrum of the chloride, and his drawings show that the agreement is rather poor. About all that can be said is that the two show bands in approximately the same regions of the spectrum, but that they differ considerably both as to intensity and more exact position.

## OBJECT OF PRESENT INVESTIGATION

The present investigation was undertaken for the purpose of determining:

1. Whether the emission bands of incandescent erbium oxide really come from the solid itself, or whether they are due to some gaseous layer very close to its surface.

2. How the three kinds of spectra given by some of the elements of the rare earths are related to each other. The three kinds of spectra are:

*a*) Absorption by solutions of the salts.

*b*) Absorption by diffuse reflection of white light from the solid compounds.

*c*) Emission by their incandescent oxides or phosphates.

The elements, erbium and neodymium, were selected partly because the absorption spectra of their solutions show a greater number of bands than those of the other elements, and also because both are known to show very well all three types of spectra mentioned above.

## APPARATUS AND METHODS

1. *Salts and solutions.*—The salts and solutions of neodymium were all made from the double nitrate of ammonia and neodymium,

[1] *Comptes Rendus*, **91**, 326–328, 376–378, 1880.

[2] *Spectres Lumineux*, Paris, 1874.

a quantity of which was kindly furnished to Professor H. C. Jones for this and other work by the Welsbach Company of Gloucester, N. J. The anhydrous chloride, sulphate, and nitrate used in making the spectrograms shown in Figs. 8 and 9 were prepared by Professor Renouf, while all the other salts and solutions used were prepared by the author, the procedure being as follows: The double salt was first precipitated by oxalic acid, and the oxalate washed thoroughly with hot water, after which it was dried and heated to a bright red until completely transformed into the bluish-gray oxide $Nd_2O_3$, a considerable quantity of which was prepared and kept on hand. From it the sulphate, chloride, nitrate, and acetate were made by simply dissolving it in the corresponding acid.

The erbium preparations used were all made from material which Professor Rowland prepared while he was interested in the separation of the rare earths. It will be remembered that while he was working on the identification of the lines in the solar spectrum he found it difficult or impossible to obtain many of the elements belonging to the group of rare earths in a state of sufficient purity for his purpose. On this account he decided to commence with the original minerals containing these elements, and make an attempt at separating the elements himself, using purely spectroscopic means to guide him in the work. Among the preparations left by him were about a dozen small bottles labelled Erbium "A," Erbium "B," etc., each one containing from two to five grams of oxide. Professor Rowland's notes do not give any definite information about the meaning of the designations on the labels, and hence the contents of each bottle was dissolved in *HCl* and made up so that all the solutions had, as nearly as possible, the same concentration. On examining the absorption spectra they were all found to be identical as far as the positions and relative intensity of the bands was concerned, but they showed some variation in absolute intensity. The examination of the spectra showed that the solutions were quite free from neodymium and praseodymium, the merest trace of the yellow band of neodymium appearing only when a syrupy solution six or more centimeters deep was used. The bands of holmium, if present at all, were not very strong, indicating that the impurities were chiefly such as give no absorption spectra, and accordingly would, in all probability, not interfere seriously

with the work of the present investigation. The preparations showing the strongest absorption bands, and hence containing the least amount of non-absorbing impurities, were selected and used in the work.

2. *Spectroscopes and photographic plates.*—For visual examination of the spectra, a small direct-vision spectroscope by Steinheil, containing a train of five prisms, was used; while for photographic purposes, a concave grating spectroscope was employed. The grating is a 2½-inch, of 1 meter focus, ruled with 15,000 lines to the inch.

Since both neodymium and erbium have absorption as well as emission bands in the red, and since the chief group of absorption bands of neodymium lies in the region between λ 5700 and λ 6300, it was very desirable to use a photographic plate sensitive to the yellow, orange, and red. Various makes of films and plates of American manufacture were tried, all of which except Cramer's Trichromatic were found to give very slight photographic action beyond λ 6100. Cramer's Trichromatic is fairly sensitive to between λ 6300 and λ 6400, but its photographic action is not very even, there being two well-marked minima in the visible spectrum.

The Wratten "Panchromatic," made by Wratten and Wainwright, of Croydon, England, was tried and found so satisfactory that it was used almost exclusively. A brief description of its properties from the standpoint of the worker in spectroscopy may not be out of place here, especially as red sensitive plates, which are at the same time sensitive to the rest of the spectrum, are not very plentiful.

The "Panchromatic" is very sensitive in the red as far as λ 7400, and in the ultra-violet at least as far as λ 2300, and it is almost uniformly sensitive throughout this region. A short exposure will reveal four faint minima at λ 4975, λ 5650, λ 6175, and λ 6675, the one at λ 5650 being much fainter than any of the others. With a full exposure it is very difficult to make out any of these minima, the action being apparently perfectly uniform. When the source is a Nernst filament the action in the red is a little more intense than that in the green or blue, while if the positive crater of the arc is used, the action is greatest in the bluish violet; this indicates a greater absolute sensibility in the bluish violet than in other parts of the spectrum, but the difference is less than in any other plate tried.

The plates are perhaps sensitive farther into the ultra-violet than λ 2300, for the spark used for comparison spectrum in the present work had no strong lines beyond this; so all that can be said is that they are about as sensitive at λ 2300 as the ordinary Eastman or Seed film. The plates must, of course, be developed in absolute darkness, for the light from the ordinary developing lantern fogs them as quickly as the light from a gas-jet fogs an ordinary plate. With this precaution and properly timing the development, there is no difficulty in getting good negatives, perfectly free from fog.

Glass plates could not be bent to the focal curve of the grating, and accordingly they were cut to such lengths (4 to 5 inches) that the definition would still be fairly good over the whole plate.

The region of the spectrum photographed was usually from about λ 3700 to λ 6700, and the dispersion in the first spectrum was such that this could be included on a plate 5 inches long. The plate-holder was movable in a direction parallel to the spectrum lines, and as the plates used were 2½ inches wide, several exposures could be made on one plate, which is indispensable when one is studying changes in the spectrum produced by variations in the conditions under which it is produced.

3. *Methods of observing the emission spectrum.*—In order to observe the emission bands of erbium oxide, all that is necessary is to dip a platinum wire in a fairly concentrated solution of the chloride or nitrate, and then hold it in the flame of a Bunsen burner. The oxide forms a more or less spongy coating over the end of the wire, and when viewed with a direct-vision spectroscope, the characteristic bands may be seen together with a considerable amount of continuous spectrum, part of which may be due to the white-hot platinum wire, but the greater portion in general to the oxide itself. The reason for this is that the spongy coating of oxide takes a very high temperature, and, as was found by Lecoq de Boisbaudran,[1] when the temperature rises the continuous spectrum increases in brilliancy much more rapidly than do the bands. In order, therefore, to see the bands to the best advantage, it is necessary to prevent the oxide from taking too high a temperature. This may be a done by making it more compact, by either one of the two following methods:

[1] *Loc. cit.*

*a*) Bend the end of a platinum wire into the form of a loop, put a small drop of a concentrated solution of the chloride or nitrate on it, and hold it in the flame. After a second or two the substance will be seen to blow out into the form of a tube generally from 2 to 4 mm in diameter and a centimeter or two long, closed at both ends. This tube is extremely thin and hence must be handled with some care to prevent breaking. It should be moistened with the solution and carefully heated again, the operation being repeated perhaps a dozen times, when it will be found that the walls of the tube have become quite thick and compact, or even that the tube has become a fairly compact solid rod, which will stand a considerable amount of rough usage, and which adheres firmly to the platinum wire. If its outer surface is very rough owing to the formation on it of very thin hollow projections, these should be removed; otherwise when the rod is heated, they will take a very high temperature, and hence give rise to the continuous spectrum which it is desired to avoid. Their presence can be readily detected, even when they do not form evident projections, by the fact that when heated they shine with a brilliant green light, quite unlike that of the rest of the rod, which is rather orange due to the bands in the red.

*b*) This method is based upon the fact that when the oxide of either erbium or neodymium in the form of a fine powder is moistened with a small amount of the chloride solution, it sets after a short time into a rather hard solid mass, a behavior very similar to that of "plaster of Paris" when moistened with water. If this mixture, before it sets, is put into a glass tube having an internal diameter of one or two millimeters, and then just as it is setting is pushed out by means of a close-fitting piston, very smooth, uniform rods of any desired lengths are obtained. A platinum wire may easily be fastened on to one of these rods by wrapping one or two turns of it around the end of the rod, and then covering it over with some of the freshly made mixture. Such a little rod, after having been carefully heated to redness, is generally rather brittle, but may be made quite tough and compact by being repeatedly moistened with the chloride solution and each time slowly heated to redness.

To observe the emission of erbium oxide when heated by cathode rays, vacuum tubes of the form shown in Fig. 1 were used. The

oxide was placed on a piece of platinum foil *A* which was situated at the focus of the concave cathode *D*. The side tube *B* was fitted to the main tube by means of a ground joint *C*, so that it was easy to take out the platinum foil *A* for the purpose of removing the coating of oxide. The wire *F* made it possible to connect the platinum foil to earth or to charge it to any desired potential.

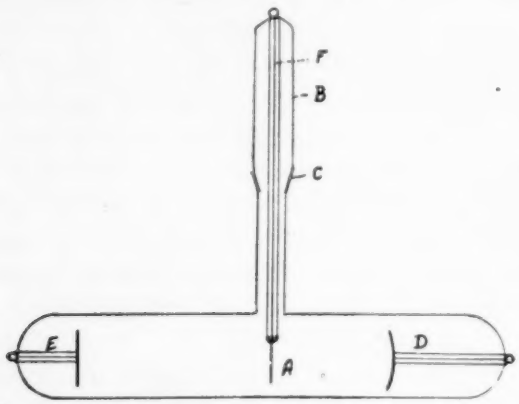


FIG. 1.

4. *Method of observing the absorption spectra.*—In order to observe the absorption spectrum of the solid salts it is necessary to focus some strong source of white light, such as the Nernst filament or the positive crater of the arc, on the dry powder, then throw an image of the spot of light on the slit of the spectroscope. For photographing the spectrum of the salts when these were at ordinary room temperatures, they were placed between two small plates of glass, held together with sealing wax; these were placed in such a position that their surfaces were parallel to the jaws of the slit. In order to avoid the light reflected from the glass surfaces, the light from the arc or Nernst filament was made to fall on the plates in such a direction that the angle of incidence was about 45°, in which case the reflected cone of light fell well off to one side. To examine the absorption spectrum when the salts or compounds were kept at temperatures above that of the room, they were spread out into a very thin layer on a piece of platinum foil, which was heated by a Bunsen burner. Various temperatures could be had by placing various thicknesses of sheet asbestos under the foil. This method was found to work satisfactorily up to temperatures of a dull-red heat. To observe or photograph the absorption spectrum at the temperature of the oxide when it is emitting, the arc was focused on the oxide while in the flame of the burner.

For observing the absorption of solutions a number of small cells were made out of a brass tube, the ends being covered by microscope cover glasses. In order to keep the solutions from attacking the brass all that was necessary, was to cover this with a thin coating of shellac.

## OBSERVATIONS AND RESULTS

1. *Emission spectrum.—a*) Erbium oxide. The important question to decide in regard to the emission spectrum is whether the bright bands are in reality due to the solid oxide itself, or are to be ascribed to some surface layer of gas, formed by the action of the flame. The simplest and most direct way of settling this would be to heat the oxide without using a flame, for example by placing it on a strip of platinum foil and heating this by passing a current through it. This was tried but no definite results were obtained, because if a thin enough layer is used to allow it to take a temperature approaching that of the platinum strip, the radiation from the layer is so feeble that it is entirely masked by that of the metal, while if a thicker coating is used it does not get hot enough. In one experiment the oxide was highly heated in an electric furnace, but here the light from the porcelain tube of the furnace was overpowering, and besides, since the oxide was practically inside a hollow vessel whose temperature was nearly uniform throughout, nothing but black body radiation was to be expected. It was therefore decided to heat the oxide by cathode rays in a vacuum. This would certainly eliminate the chemical action of the flame, but would still leave the reducing action known to be a property of cathode rays. The method has, however, one great advantage over any flame, and that is that by controlling the vacuum and current-strength, the oxide may be heated to any desired temperature, from that of the room to the most intense white heat, and so is very well suited for the purpose of studying the change in the emission with temperature. As the oxide is heated gradually under the bombardment of cathode rays, the following may be observed:

At temperatures below red heat it gives out a greenish-yellow light, the so-called fluorescent spectrum, already studied and described by Crookes.[1] As the temperature rises the emission

[1] *Proc. R. S.*, **40**, 77–79, 1886.

bands in the green soon become visible, and almost simultaneously the bands in the red are seen. The bands in the red always have a considerable amount of continuous spectrum near them, while at low temperatures the bands in the green stand out from a relatively very dark background. With rising temperature the bands in the blue soon become prominent, and the continuous spectrum increases in intensity; simultaneously the bands become more and more hazy, and finally, when the temperature becomes very high, nothing is seen but a perfectly continuous spectrum. At this stage the oxide shines with a light as brilliant as that of a Nernst filament. These appearances were the same whether the platinum strip upon which the oxide was placed was connected to earth, or charged to a high positive potential by being connected to the anode. They were also the same when it was charged to such negative potentials as it was found possible to employ without disturbing the paths of the cathode particles too much. Usually when a negative potential of more than a hundred volts was employed, Wehnelt discharges of slowly moving cathode rays took place which seemed to come from isolated points of the heated oxide rather than from the whole surface. It is possible that the starting-points of these Wehnelt discharges were particles of such impurities as calcium, sodium, or potassium.

When one of these tubes had been used for a few hours, its walls near the strip covered with the oxide became coated with a black deposit. This was at first thought to be platinum, but was shown not to be that by the fact that it could not be dissolved by aqua regia, even when this was boiled in the tube. The only way found to remove the deposit was to scour it out mechanically by means of sand and water, although all the common acids were tried. The deposit was in all probability the metal of the oxides, these being reduced by the action of the cathode rays.

The emission of the oxide when heated in a cyanogen flame was also examined, and found to be identical with that observed when heated in a vacuum, by cathode rays, or when heated in a Bunsen flame. The object of using the cyanogen flame was to eliminate the reducing action of hydrogen.

*b*) Neodymium oxide. When neodymium oxide is heated in a Bunsen flame it gives a spectrum consisting of two extremely wide,

hazy bands, the intensity-curve of which is shown in Fig. 2. If, however, the oxide be present as an impurity in erbium oxide, it gives a fine series of bands in the yellow and orange, a photograph of which is shown in Fig. 3. It was also introduced as an impurity in calcium oxide, but the bands in this case were very much hazier; that is, the spectrum approached much more nearly that of the pure neodymium oxide.

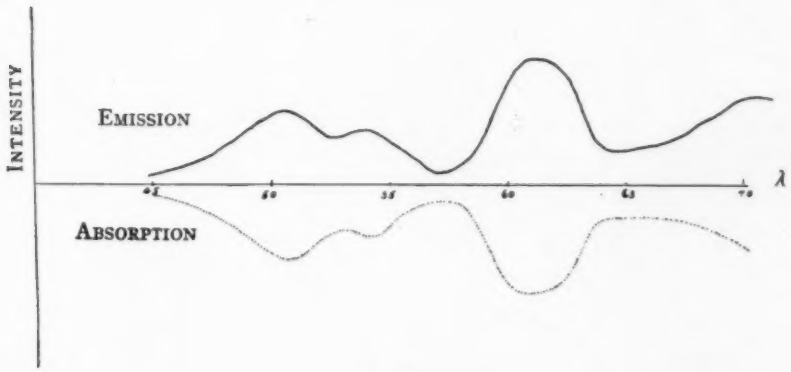



FIG. 2.

2. *Conductivity of erbium and neodymium oxides at high temperatures.*—According to a theory advocated by J. Stark, continuous spectra are due to the free electrons in a substance, and hence we should expect that unless a substance has an appreciable conductivity it should not radiate a continuous spectrum. At temperatures of 1200° C. or below, the continuous spectrum in the light emitted by a bead of erbium oxide is very faint, much more so than is the case with neodymium oxide. It was accordingly of some interest to get at least some relative values of the conductivities of these oxides at high temperatures.

The oxide was made into the form of a Nernst filament by the method already described above. The filaments actually used were about 15 mm long by 2 mm in diameter, and were very compact. This was ascertained by breaking each one after the measurements had been completed; the broken ends showed a very fine-grained structure like that of broken porcelain. They were heated by means of a small platinum furnace, the temperature of which was deter-

mined from resistance measurements made on the heating coil itself.

The conductivity of the filaments was determined by measuring the current through them when an E. M. F. of from 2 to 110 volts was applied; the current being measured by means of a d'Arsonval galvanometer (sensibility $= 2.3 \times 10^{-8}$ amperes).

The following are a few of the values found:

SPECIFIC RESISTANCE

| Temperature | Neodymium Oxide | Erbium Oxide |
|---|---|---|
| 1400 C. | 1,860 ohms | 20,000 ohms |
| 1275 C. | 4,000 " | 100,000 " |
| 1150 C. | 7,500 " | 200,000 " |

No great accuracy is claimed for these values, the object being rather to find comparative values for the two oxides, than absolute values. They show, however, that at the temperatures given, erbium oxide is a very much poorer conductor than neodymium oxide, and if, as is very probable, the emission of a continuous spectrum is due to the presence of a large number of free electrons, this might suggest an explanation of the fact that neodymium oxide when present as an impurity in erbium oxide emits the bands much better than when by itself. The amount of neodymium oxide needed to give the bands to the best advantage is very small, perhaps less than one per cent., so this would not lower the resistance of the erbium oxide very much.

3. *Absorption by solid compounds.—a*) Erbium oxide. It was stated by Crookes[1] that if a bead of erbium oxide is illuminated with white light and examined with a spectroscope, a group of very fine lines is seen in the green, and he gives a diagram showing the positions of these lines.

Besides this group in the green, there is one in the red, one in the blue, and two in the violet, and also a number of fainter bands in various parts of the spectrum. The intensity of the absorption bands was found to vary considerably with the treatment previously given to the oxide. The three spectrograms reproduced in Plate VIII, Fig. 4, illustrate this. The first (*a*) is the result of an exposure to the light diffusely reflected from the oxide in the powder form, obtained by heating the oxalate; the oxide used in getting the second (*b*) was

[1] *Loc. cit.*

# PLATE VIII

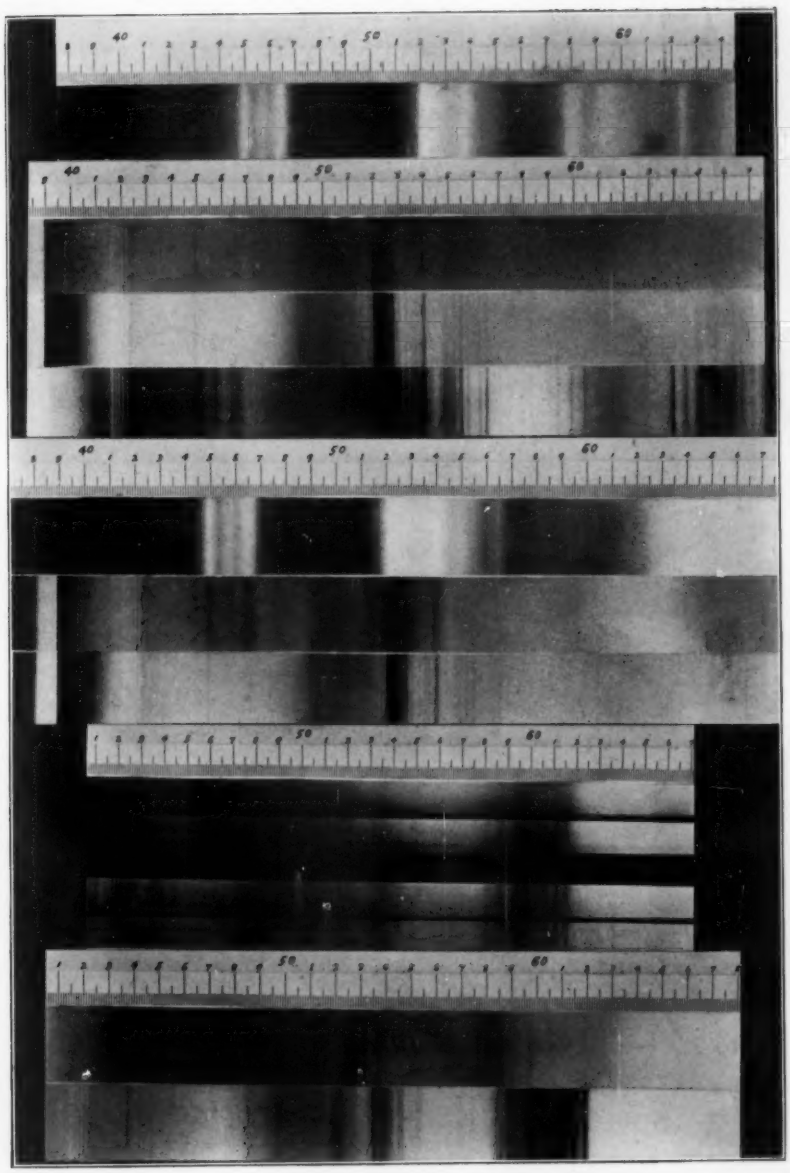



FIG 3

FIG 4

FIG 5.

FIG 6

FIG 7

in the form of a rod which was made from the chloride solution by the first method described above. It had been heated in the Bunsen flame for at least one hundred hours before this spectrogram was taken. The third spectrum (*c*) was made by employing a rod made according to the second method described above, the rod having been heated in an oxyhydrogen flame for a length of time sufficient to make its surface appear as though it had begun to fuse. The great change in intensity may be explained by the following considerations:

In order that the light diffusely reflected from the solid salts may show absorption bands, it is, of course, necessary that it should have passed through some of the particles of the salt, that is, the light in which the absorption is observed is really transmitted light.

The intensity of the absorption bands will therefore be increased if the length of path traversed by the light in the substance is increased. Now, the fused oxide is probably fairly transparent, for when little rods of it are held in the electric arc for a moment, then withdrawn and allowed to cool, their surface presents a distinctly glassy appearance, which, when held in sunlight and viewed with a spectroscope, shows hundreds of very dark absorption lines or bands. The spectrum is identical with that shown in Fig. 4, *c*, only the bands are very much more intense, and hence a number that are too faint to be seen in the spectrogram, here show quite distinctly. Attempts were made to photograph the spectrum from these fused or glassy surfaces, but it was found so difficult to avoid streaks of continuous spectrum due to reflection from the surface itself, that it was given up.

Returning now to the spectra shown in Fig. 4; when the oxide is in the form of a very fine powder the length of path traversed by the light in the substance itself before it emerges, must be limited to the distance through a very few particles at most, and accordingly, as might be expected, only the strongest absorption bands would be seen. In the second case, where the oxide had been kept at a high temperature for a very long time, incipient fusion had undoubtedly taken place to some extent which would lengthen the path of light in the substance considerably. In the third case the fusion had progressed much farther, although the surface had not assumed the glassy appearance which it gets when the fusion is complete.

It was noticed that the chief groups of absorption bands agree approximately in position with the emission bands when the oxide is heated, and it was natural to assume that the absorption spectrum changes with temperature in such a manner as to become identical with the emission spectrum when high temperatures are reached. This was tried and found to be the case. Fig. 5 shows photographs of the emission spectrum (*a*), absorption spectrum of the oxide while in the flame (*b*), and absorption spectrum of the oxide at ordinary room temperatures (*c*). Visual observations showed that when the temperature is gradually raised the absorption bands became hazy and broaden out, finally running together into the broader bands corresponding to those of the emission spectrum. The individual bands are affected quite differently, as may be seen by noting the changes in the two principal groups in the green. The strongest band in the most refrangible group, as well as the band on its violet side, is shifted toward the red, while the chief band in the less refrangible group is not shifted at all.

The group of bands in the blue is also shifted toward the red somewhat, as is also the group at λ 3780 just beyond the cyanogen bands.

*b*) Neodymium oxide. The changes produced by change in temperature are also well marked in the case of the absorption of neodymium oxide. These are illustrated by the photograph reproduced in Fig. 6. The first spectrum in the figure shows the absorption of the bluish-gray oxide at a temperature somewhat below 100° C.; the second shows the same for a temperature of about 200°; the third for a temperature of about 400°, and the last one for a temperature of about 600° or a dull-red heat. None of the bands here shows any appreciable shift, but the changes in intensity are in some cases very striking. Consider the fine group of bands lying between λ 6200 and λ 5830. For convenience in speaking of them, they will be referred to by the letters *a*, *b*, *c*, *d*, *e*, *f*, *g*, *h*, and *j*, beginning at the red. Near room temperature, *a*, *b*, and *c* are of nearly equal intensity, *c* being if anything slightly the more intense; *e* and *f* are of about equal intensity, so also *g* and *h*, while *j* is rather more intense than *h*. At 200° C., all the bands have widened somewhat, and the changes in intensity are about as follows: *c* has decreased very much, its intensity being

distinctly less than that of *a* and *b*, which are still equal; *d* has almost disappeared; the intensity of *f* is less than that of *e*, that of *h* very much less than that of *g;* while the intensity of *j* has decreased to less than one-half of its value at the lower temperature. A glance down the spectrum toward the violet shows that the group comprised between λ 4800 and λ 5500 has practically disappeared with a temperature-change of only a little more than 100° C. The bands at λ 4475 and λ 4427 have changed scarcely at all, while that at λ 4382 has had its intensity reduced to about half-value.

At 400°, the bands have widened still more. *a* and *b* are now the most prominent bands in the yellow group, with *b* slightly more intense than *a*, *c* is not specially conspicuous, while *d* can be seen only with difficulty; *e* is much more intense than *f; h* can no longer be distinguished, appearing now only as a slight shading on the violet edge of *g; j* is becoming very faint and hazy. The blue bands at λλ 4475, 4427, and 4382 have changed very little in intensity, but have broadened somewhat.

At 600°, *a* is rapidily losing its identity, while *b* is still fairly distinct; *c*, *d*, *e*, and *f* have run into one band with an intensity maximum corresponding with the position of *e*. The band due to *g* and *h* has become very hazy and faint, while *j* can be seen only with difficulty. The three blue bands are still fairly distinct.

At the temperature which the oxide takes when held in the flame of the Bunsen burner the absorption agrees exactly with the emission as shown by the dotted curve in Fig. 2.

When rods of neodymium oxine are heated in the arc, or in the oxyhydrogen flame, the surface fuses as in the case of erbium oxide. The fused surface is, however, almost jet black, indicating that fused neodymium oxide is much less transparent than that of erbium When sunlight is focused on the surface of this oxide, the bands may be seen, but they are so nearly drowned out by the admixture of white light reflected by the surface itself, that they are seen no better then when the fine powder is used. If the fused oxide could be made into very thin plates these would undoubedly be transparent enought to allow the absorption spectrum to be seen with increased intensity, since by this method the reflected light would be very nearly eliminated.

It is stated in chemistries[1] that the oxide of neodymium ($Nd_2O_3$), if not heated too strongly, is pinkish in color, while if heated to a bright red it turns to a bluish-gray color. Some of the pink oxide was examined and was found to give an absorption spectrum which is quite different from that given by the gray oxide. Fig. 7 shows the two spectra compared. By heating the pink oxide to a bright red it changes into the gray variety. An attempt was made to prepare this pink oxide from the oxalate by heating it very gradually in an electric furnace; but nothing could be obtained except the gray oxide. Similar results were obtained when starting with the chloride, nitrate, or sulphate; at more or less elevated temperatures they change into the gray oxide, and at no stage could even a trace of the bands of the pink oxide be found. It would be interesting to know whether the pink oxide really has the same formula ($Nd_2O_3$) as the other variety, and if so, what the molecular differences are which cause such a marked change in the absorption.

*c*) Other compounds. The spectra of a number of compounds of both neodymium and erbium were observed both visually and photographically. These compounds were the chloride, oxychlorides, nitrate, subnitrates, sulphate, oxalate, and acetate of neodymium, and the nitrate, oxalate, and sulphate of erbium.

Fig. 8 shows the spectra of the chloride, nitrate, sulphate, and oxalate of neodymium, the salts being all dry. These illustrate quite well the fact that the absorption is different for the different compounds. There is, however, a general resemblance among the spectra shown in Fig. 8 (Plate IX). The group of bands in the yellow, for example, although different in structure in the different compounds, still occupies about the same position, and if viewed in a spectroscope of low dispersion might easily be thought to be the same in the four compounds. The same holds for the double group in the green.

Even this general resemblance disappears in some of the other compounds. If the chloride is heated in air it first changes into an oxychloride, and this finally into the gray oxide. The spectra of these three are shown in Fig. 9. It will be seen that the group of bands in the yellow seems to move toward the red as we pass from the chloride to the oxychloride to the oxide. Similar changes may

[1] O. Dammer, *Handbuch der anorganischen Chemie*, Vol. IV, p. 648.

be noticed for some of the other groups. Such changes are also noticed when the nitrate is heated so as to change into the subnitrate, and these into the gray oxide. This apparent "motion" of a "group of bands" may perhaps be what Becquerel refers to in the quotation cited above. On closer examination, however, it becomes evident that we are not dealing with the motion of a group as a whole, for the arrangement of the bands in the displaced group is very different from those in the original.

It may be a little difficult to say just what is meant by saying that a group of bands moves as a whole. Motion implies a continuous change of position, such as we have, for example, in the temperature change in the absorption bands of erbium oxide. Here we have nothing of that kind, for what actually takes place is this: the molecules of $NdCl_3$, for example, are capable of absorbing certain wave-lengths, which may, to be sure, vary slightly with temperature; similarly, the molecules of the neodymium oxychloride which is formed when the chloride is heated in air, are capable of absorbing certain wave-lengths, which will in general be different from those absorbed by the chloride. If the spectrum is observed while the chemical change is taking place, both sets of bands are found to be present, those belonging to the chloride gradually decreasing in intensity, while those belonging to the oxychloride increase until, when the chemical change is complete, the chloride bands have entirely disappeared. Unless a group of bands in the oxychloride corresponds band for band with a similar group in the chloride spectrum, we cannot very well say that we are dealing with the same group, for it is probable that the individual bands in the two cases are due to different vibrators.

The narrow band near $\lambda$ 4270 shown by aqueous solutions of neodymium salts is interesting in this connection. It appears in very nearly the same position in solutions of the sulphate, chloride, acetate, and nitrate. In the nitrate it is, however, double, and in the solution of the acetate it is wider than in solutions of the chloride or sulphate. In the dry salts a narrow band appears in about the same region, the wave-length being in general somewhat greater. In the oxalate, for example, there is a band at $\lambda$ 4300; in the chloride there is also a strong band at about $\lambda$ 4300, but there are besides three fainter bands near it, which are equally narrow, one of which falls at

about λ 4280. In the oxychloride referred to already there is no band near λ 4300, but there are four very narrow bands beginning at about λ 4370, and extending toward λ 4425. The pink oxide has a band at about λ 4310, while the gray oxide has no band before we get to the red side of λ 4375. In view of these facts we cannot be sure that the band λ 4270 seen in solutions is found shifted toward the red in all dry compounds, for we may be dealing with entirely different bands.

*d*) Crystals. As stated above, Becquerel found that the absorption spectrum of a crystal depends somewhat upon the direction in which the (polarized) light is passed through it. This was also observed in the case of neodymium nitrate crystals in this work. Light was passed first through a nicol and then through a flat plate of $Nd(NO_3)_3$ about 2 mm in thickness. In a given position of the nicol some bands were seen which entirely disappeared if the nicol was turned through 90°. The reason for this is of course that the crystals are doubly refracting and the absorption is different in the two rays. This was seen in a very striking manner in a small crystal of erbium chloride. The crystal was in the form of a small prism having a refracting angle of about 30°. When light was passed through this prism, the ordinary and extraordinary rays were separated very nearly as widely as they are in an Iceland spar prism of the same angle. The absorption in the two rays was seen to be quite different. Unfortunately the crystal melted before a determination of its optic axis could be made, but polariscopic observations on both chloride and nitrate of erbium and neodymium indicate that the double refraction of these substances is at least twice as great as in Iceland spar.

If the spectrum of a crystal is compared with that of the corresponding dry salt, we still find some differences, but they are very slight compared to those mentioned above. Fig. 10 shows the change in the absorption of erbium sulphate crystals when these are heated more and more: that is, when the water of crystallization is driven off. (The sulphates of both neodymium and erbium part with their water of crystallization without decomposition, by simply being heated in the open air.) The change illustrated in Fig. 10 is very similar to that due to temperature in the case of erbium oxide. The bands due to the crystals are wider than those of the dry salt, and are also

# PLATE IX

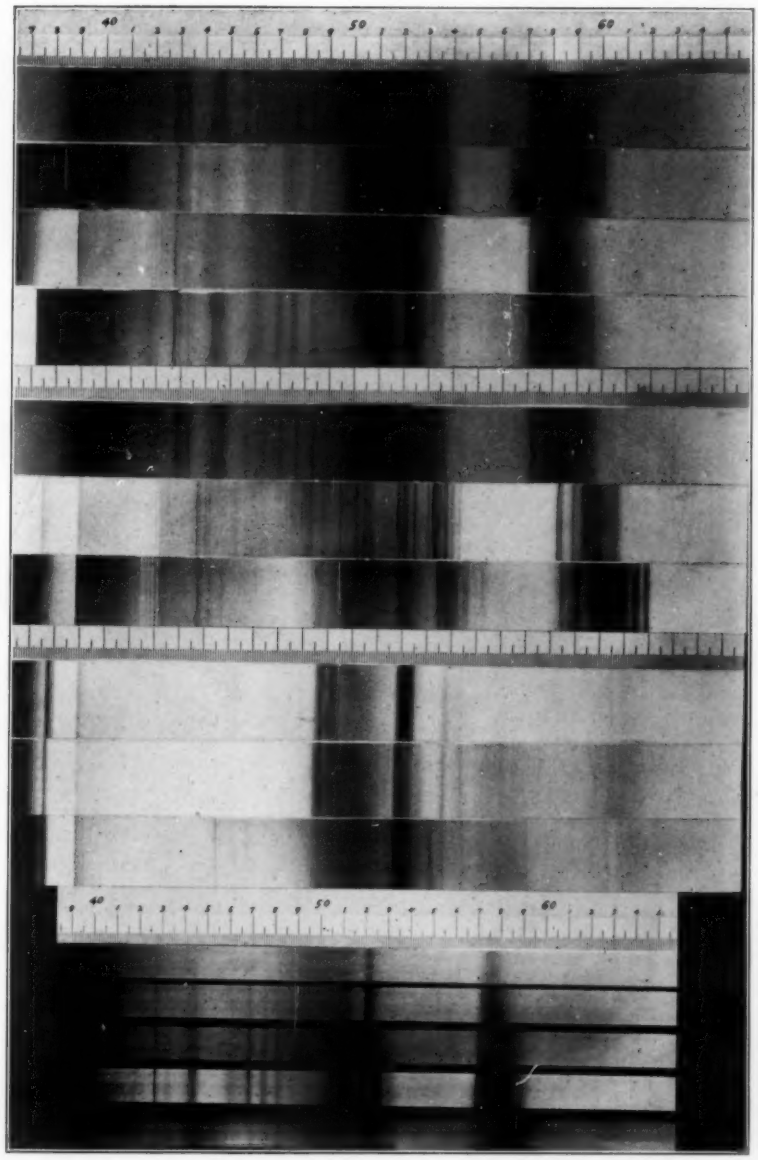



FIG 8

FIG. 9.

FIG 10.

FIG 11.

somewhat displaced toward the red. The displacement toward the red is also shown by neodymium sulphate, but the difference in width and general appearance of the bands is not very marked.

4. *Absorption of solutions.*—So much work has already been done on the absorption spectra of solutions of neodymium and erbium, that little attention was given to them in this work; it seemed, however, of some importance to compare the spectrum of a solution directly with that of the crystals obtained from it; and accordingly the spectra of solutions of the chloride, nitrate, sulphate, and acetate in various concentrations and those of the corresponding crystals were photographed to the same scale so that comparisons could be made with ease. Fig. 11 shows the absorption of an aqueous solution of the sulphate of neodymium in concentrations varying from $\frac{1}{8}$ normal to $\frac{1}{64}$ normal, compared with the absorption of the crystals deposited from the stock solution of sulphate. The general resemblance between the spectra is very apparent, but there are, however, differences especially well marked in the group in the yellow. In the crystals this group is seen broken up into individual bands, while in the more concentrated solutions, although the width of the group is smaller, the bands are not separated. In the $\frac{1}{32}$ normal solution the yellow group is seen broken up into four or five bands, whose positions are, however, different from the bands seen in the spectrum of the crystal. A $\frac{1}{16}$ normal solution of either the chloride or the nitrate shows the group broken up exactly as it is in the sulphate solution, although, as we have seen above, the bands in this group, in case of the crystals of the nitrate and chloride, are quite different.

Speaking very generally, it may be said that the spectra of solutions of different salts are nearly alike, while the spectra of the dry salts are very different. The spectra of the crystals seem to be, as it were, intermediate, differing from the two extremes much less than the extremes differ from each other.

## DISCUSSION OF RESULTS

It has been shown that the absorption of the solid oxide at high temperatures corresponds exactly to the emission at the same temperature in accordance with Kirchhoff's law. This shows that the emission and absorption of the oxides, and presumably also of the

phosphates, are really both due to the same vibrators. The absorption of the oxide is very similar to that of other solid compounds, so that it is reasonable to suppose that the mechanism of the absorption spectrum of all solid compounds is the same. The general resemblance between the spectrum of a dry salt, the crystals, and the corresponding aqueous solution indicates that these are also due to the same thing. It seems reasonable therefore to assume that the three kinds of spectra defined above are due to the same vibrators, and there remains only to find the causes which produce the variations which are observed.

Let us assume that the vibrators in question are electrons located inside the metallic atom; these electrons are held in positions of equilibrium by forces due partly to the positive charge of the atom itself and partly to the other electrons inside it. It is evident that an atom consisting of a region positively charged and having in it a number of electrons whose combined charge is sufficient to neutralize the positive charge, although neutral for a point far away from its center, will still exert forces on charged bodies near it; or, we may say, the electric field of a Saturnian atom vanishes for points far removed from the atom, but not for points in its immediate neighborhood. It is also evident that the field in the immediate neighborhood will be different for atoms of different substances.

Now, to fix ideas, let us consider a neodymium atom having inside it certain electrons which may be set in vibration by light-waves falling upon them. If an atom of another substance such as chlorine is brought very near to it, the electric field of the chlorine atom will affect the periods of these electrons. It is also to be expected that an oxygen atom will produce a different change in the period, since its electric field is undoubtedly different from that of the chlorine atom. This indicates why the different compounds should show different absorption spectra.

To explain the temperature change, which, as we have seen, consists chiefly of a widening of the bands, we have only to consider that the periods of the vibrators will be a function of the distance between the disturbing atom and the atom containing the electron. If this distance is continually varying, that is, if the two atoms are vibrating with reference to each other, the period of the electron will also be

changing; in other words, the absorption it occasions will be a band rather than a line. Now, with increasing temperature the oscillations of the atoms in a molecule have their amplitudes increased and hence we should expect the bands to widen.

That the presence of water of crystallization should produce a change similar to that of raising the temperature indicates that the presence of water molecules diminishes the forces holding together the atoms forming the molecule, thus increasing the amplitudes of the oscillations; this is also what might be expected when it is considered that water has great dissociating powers, which depend primarily upon diminishing the forces holding the parts of a molecule together.

The fact that the spectra of aqueous solutions of different salts of the same element are so nearly alike may be due partly to the fact that the salts are dissociated, and hence the metallic ion is surrounded by water molecules, and hence would be in almost the same condition, no matter what salt is dissolved. It is also probable that even if the molecule of the dissolved salt is not dissociated, the effect of the molecules of the solvent in modifying the periods of the vibrating electrons would be very great.

## SUMMARY

The results may be summed up in the following statements:

1. The bright band emission spectra of the oxides of erbium and neodymium are due to the oxides themselves, and correspond exactly to their absorption at the same temperature.

2. The absorption of the solid compounds changes with temperature, the change consisting in a widening of the bands, and in some cases a shift toward the red, as the temperature is increased.

3. The absorption spectra of dry compounds are different for different compounds of the same element.

4. The presence of water of crystallization in a compound seems to change its absorption in the same way that a rise in temperature does.

5. The results are satisfactorily accounted for by assuming that the vibrator responsible for the spectra is the electron inside the metal-

lic atom, its period of vibration being affected by the presence of other atoms or molecules.

In conclusion I wish to thank Professor Ames, who suggested the work, and under whose direction it was carried out, for his unfailing interest and many valuable suggestions.

JOHNS HOPKINS UNIVERSITY
June 1907

# PHYSICAL NATURE OF METEOR TRAINS

By C. C. TROWBRIDGE

Meteor trains are luminous clouds formed by meteors which persist long after the incandescent nucleus has disappeared. They not infrequently remain visible to the naked eye for many minutes, and in a number of well-authenticated instances have been observed to last even as long as three-quarters of an hour. From a study of many recorded observations it is evident that meteor trains seen at night are self-luminous, and are sometimes bright enough to be seen several hundred miles distant. The trains vary from ten to even thirty miles in length when first deposited and rapidly expand in width, and those that are visible for over ten minutes are usually found to be a mile or more in diameter.

*Previous investigations on the subject.*—Meteor trains, or "persistent streaks," as they are often called, have been observed by many astronomers, but the cause of their luminosity is still regarded as an unsolved mystery. Only a few papers have been published which deal directly with the subject, but there are many which contain careful records of observations of trains incidentally seen by meteor observers while engaged in mapping radiant points and in the study of other problems of meteoric astronomy.

J. Ennis has described seven different trains[1] seen by various persons, and E. E. Barnard has published a paper on the drifts of five trains observed by him at Nashville, Tenn.,[2] in which also he calls attention to the importance of the phenomenon. While in a few other papers the subject has been referred to in a general way, no systematic attempts to collect the records together appear to have been made hitherto. It is the belief of the writer that valuable facts concerning the earth's atmosphere can be obtained from a study of the records which already exist. With this end in view a catalogue of meteor trains has been compiled and the records made the subject of a comparative study for several years. At the same time the writer has made a study of gas phosphorescence in the laboratory.

[1] *Proceedings of the American Association for the Advancement of Science*, 1871.

[2] *The Sidereal Messenger*, 1, 174, 1883; 10, 426, 1891.

*The reliability of the records.*—The observations of meteor trains have been made chiefly by well-known astronomers at astronomical observatories, or by trained meteor observers, who have recorded the facts in scientific journals. Most of the observations have been made since 1860. They are complete in many cases; while in others only a few details are given. The greater part are trustworthy and scientific records. Among the astronomers who have made observations are the following: In England: Denning, Herschel, Corder, Greg, Backhouse, Booth, etc.; In the United States: Twining, Newton, Kirkwood, Young, Barnard, Gilman, etc.; In other countries: Schmidt, von Niessl, von Konkoly, Schiaparelli, etc. A systematic study of these records is a work of no little magnitude. The observations which have formed the basis of the writer's comparative study of the trains are chiefly those made in England and the United States, but it is intended to take up later all records that can be found, including those in other countries. The facts given in this paper are therefore only a portion of the available records, and are necessarily of the nature of a preliminary report, but they are of sufficient interest to warrant their presentation at this time. About 175 observations have been studied of trains having a duration which positively identified them with the phenomenon under discussion. The subject is treated under the following heads:

1. Altitude of meteor trains.
2. Color of meteor trains.
3. Visible duration of meteor trains.
4. Explanation of the meteoric glow or "auroral light."
5. Probable explanation of the dual appearance of trains.
6. Diffusion of meteor trains.
7. Drift of the atmosphere at great altitudes.
8. Resemblance of the meteor train to the afterglow produced by the electrodeless ring discharge.
9. Summary of the chief results obtained.

## I. ALTITUDE OF METEOR TRAINS

The determination of the height at which meteor trains occur is important, not only in establishing the altitudes of atmospheric currents shown by the drift of the trains, but also because it may throw

light on the physical cause of the phenomenon. It is the purpose of the writer to show that meteor trains that are observed at night occur at a very definite altitude, and furthermore that there are various facts which indicate that the formation of the train is due rather to the state of the earth's atmosphere where the train is formed than to the constitution, size, or condition of the meteor itself.

The observations on the altitude of meteor trains have been very accurately made in a few cases and approximately made in a number

TABLE I

ALTITUDE OF THIRTEEN METEOR TRAINS OBSERVED FROM TWO OR MORE STATIONS MANY MILES APART

| Catalogue Number | Altitude Limits of Visible Track of Nucleus—Miles | | Altitude Limits of Train—Miles | | Mean Altitude of Train—Miles | Altitude Computation Made by |
|---|---|---|---|---|---|---|
| | Beginning | Ending | Beginning | Ending | | |
| 10 | | | | | 50 | A. S. Herschel |
| 12 | 100 | 53 | 59 | 53 | 56 | A. and J. Thompson |
| 26 | | | | | 54 | A. S. Herschel |
| 29[1] | 120 | 60 | 65 | 60 | 63 | H. A. Newton |
| 44 | 68 | 49 | 59 | 49 | 54 | H. A. Newton |
| 46 | | | | | 51 | H. A. Newton |
| 47 | 65 | 52 | | | 58 | H. A. Newton |
| 52[2] | | | | | 59 | H. A. Newton |
| 80 | 90 | 30 | 58 | 50 | 54 | W. F. Denning |
| 120 | 78 | 47 | 59 | 47 | 53 | W. F. Denning |
| 121 | 65 | 37 | 57 | 45 | 51 | W. F. Denning |
| 125[3] | 65 | 28 | | | 45 | W. F. Denning |
| 129 | 90 | 41 | | | 54 | A. S. Herschel and Greg |
| Mean | 82.8 | 44.1 | 59.5 | 50.7 | 54.0 miles =87.0 km. | |

[1] "Over sixty miles"—train five miles long, carefully calculated.
[2] Altitude of lower part of train.
[3] Short train ½° long at forty-five miles.

of others. Table I contains the heights of thirteen trains seen at night, which were observed from two or more stations widely apart. In some cases ten or fifteen simultaneous observations were made. The table gives the altitude of the trains above the surface of the earth in miles. The average of the heights above the surface of the earth of the middle portion of the trains is 54.0 miles or 87.0 kilometers. In a previous paper by the writer[1] among the altitudes for meteor trains given were several greater heights than any of those in Table I, but these have now been discarded because, on studying the

[1] "Abstract," *Physical Review*, **24**, 514, June 1907.

original records, it was found that the figures given referred to the meteor track and not the train.

The position of eight meteor tracks with their accompanying trains with respect to the earth is shown in a chart, Fig. 1. They are drawn approximately to scale for length of path, altitude of train,

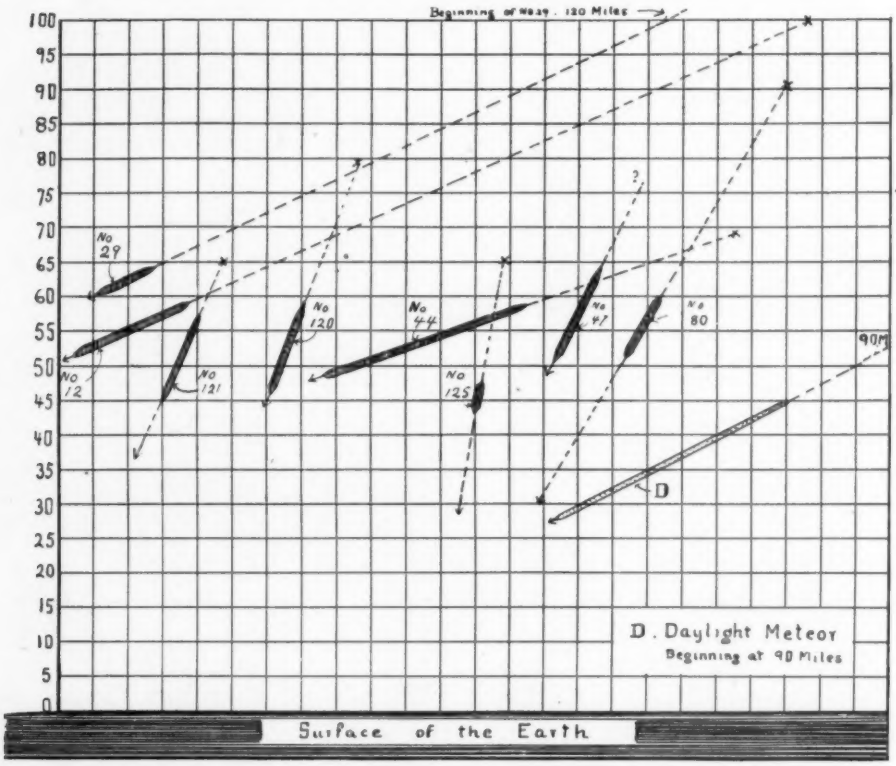



FIG 1.—Chart Giving the Altitude of Eight Self-luminous Meteor Trains and the Corresponding Lengths of Meteor Tracks.

and as near as possible angle of flight to accord with the recorded length of train. In all cases the meteors were observed at two or more stations and the heights, etc. were calculated by either W. F. Denning or H. A. Newton, except in one case.

No. 29, Yale Observatory, New Haven, Connecticut, November 14, 1866, 2:11 A. M. (many observations). Altitude of track, 120 to 60 miles; "train over sixty;" visible nine minutes; calculations by H. A. Newton.

No. 44, Yale Observatory, New Haven, Connecticut, and many other observatories, November 14, 1868, 1:12 A. M. Train extended from 59 to 49 miles altitude, and was 30 miles long at first; remained visible 44 minutes; calculations by H. A. Newton.

No. 80, observed in central England, August 26, 1894, 10:20 P. M. D. E. Parker and others; calculations by Denning; 90 to 30 miles; length of path, 66 miles; train 8 miles long, center being at 54 miles altitude; visible for 30 minutes.

No. 120, Leeds and Bristol, England, August 13, 1888, 11:33 P. M., observed by Denning and others. First appearance at 78 miles; extinction at 47 miles; train extended 18 miles from 59 to 47 miles altitude.

No. 121, Bristol and Sunderland, Eng., November 14, 1888, 5:19 A. M.; F. W. Backhouse and Denning. The meteor appeared at 65 miles altitude and disappeared at 37 miles over the North Sea. The train extended from 57 to 45 miles.

No. 12, Cardiff and Sidmouth, England, November 14, 1866, 1:08 A. M. At beginning 100, at ending 53 miles; length of streak, 16 to 18 miles at the lower end of the meteor's track.

No. 47, Eastern United States, November 14, 1866, 2:48 A. M. See Fig. 4.

No. 125, Bristol and Stonyhurst College, England, December 4, 9:17 P. M. A short streak at 45 miles altitude; calculations by Denning.

It appears probable from the chart, Fig. 1, that the altitude above the earth at which the persistent train is formed does not depend on the height at which the nucleus begins to glow. Interesting cases in favor of this point are meteors Nos. 12 and 29, which traveled forty or fifty miles as bright incandescent nuclei before the train zone was reached where trains were deposited. The nuclei of Nos. 44 and 80 traveled over twenty-five miles before the point was reached where the trains were formed. In the report of the Luminous Meteor Committee of the British Association for the Advancement of Science, 1867 (p. 405), among the records of observations of the shower of November 14, 1866, from different stations are the following accounts showing that the meteor trains in general were deposited only along a portion of the meteor track. Mr. Greg, reporting from Manchester and referring to the meteors and train, stated that "in the case of the larger ones with disks of 2′ or upwards the nucleus seemed finally to emerge from, or to shake off, or lose the phosphorescence for the space of a few degrees and then vanish." Mr. Glover, reporting from Chesham, stated "in nearly every instance the head ceased to emit a train before it vanished." Also Mr. Goulier at Metz reported that "a remarkable peculiarity of the meteors was that the streaks

were shorter than the entire length of their course, the nucleus shooting ahead of the train for some space without emitting the phosphorescent light of the streak."

From the foregoing facts it is evident that trains seldom if ever occur below 45 miles altitude or over 65, the usual height being between 50 and 60 miles (80 to 100 km), which agrees with a statement previously made by W. F. Denning. In this zone 50 to 60 miles above the surface of the earth there seem to be conditions which are favorable to both the formation and the persistence of the mysterious luminosity of the meteor trains. The condition of a gas which is most important in the production of electrical discharges, and in the formation glows is gas pressure. It is very probable, therefore, that the pressure of the atmosphere prevailing from 45 to 65 miles of altitude is such that self-luminous trains can be formed and be visible between those heights only. Fifty-four miles (87 kilometers) appears to be the altitude which is most favorable for longest visible duration.

## II. COLOR OF METEOR TRAINS

The colors of meteor trains show a good deal of variation according to the published observations. Among the colors recorded are red, orange yellow, yellow, emerald green, blue, silver, and also white. In the accompanying tables the trains seen in darkness are separated from those shining by the reflected light of the sun and the two sets show a marked difference. The observations used in the tables are only those where very definite statements were made, and those of trains which persisted with a few exceptions longer than a minute. This eliminated the possibility of confusion of the color of the train proper with that of the nucleus, or with that of the mass of sparks which sometimes persists for a few seconds in the track of a meteor.

Among the trains observed at night, in Table II, in several cases green trains changed gradually to white, and in one instance from greenish to a "dull reddish or warm color." Out of the twenty-seven self-luminous trains, twelve were of various shades of green, and eleven either bluish, silver, or white. If, as in several cases observed, the trains change from green to white, a number of white-appearing trains are to be expected in the case of green trains of a low degree of luminosity. Many of the trains in Table II were those formed by

Leonid meteors, the trains of which are usually green, while those left by the Perseid meteors are more likely to be yellowish. The self-luminous meteor train of long duration therefore appears to be a light of fairly consistent hue. If the phenomenon is a gas phosphorescence a slight change in the constitution of gas in the train would no doubt alter the color somewhat, for the color of gas phosphorescence has been found by H. F. Newall to vary for different combinations of gases.[1] Train No. 26 in Table II was reported

TABLE II

COLOR OF METEOR TRAINS OBSERVED AT NIGHT (SELF-LUMINOUS)

| The Author's Catalogue Numbers | Color | Number of Trains |
|---|---|---|
| 19, 125 | Orange | 2 |
| 26 | Yellow | 1 |
| 15, 21, 28, 32, 41, 42, 45, 80, 85, 87, 88, 95 | Green, emerald green, or bluish green. | 12 |
| 12, 43, 44 | Blue (also greenish blue) | 3 |
| 13, 27, 39, 62 | Silver or grey | 4 |
| 10, 117, 123 | White | 3 |
| 71 (changed from) | "*Red* to bluish"[1] | 1 |
| 89 (changed from) | "Greenish to dull reddish,[1] or warm color." | 1 |
| Total | | 27 |

[1] Red probably refers to track of sparks.

in a catalogue of meteors as having an orange-red train, but according to the original paper the correct record is "a pale-yellow cloud." Red was not mentioned.

The eleven trains in Table III were in sunlight. Most of these

TABLE III

COLOR OF METEOR TRAINS (ILLUMINATED BY SUNLIGHT)

| The Author's Catalogue Numbers | Color | Number of Trains |
|---|---|---|
| 74, 116 | Red | 2 |
| 70, 82, 111 | Pink | 3 |
| 3, 31, 93 | White | 3 |
| 40 (11:40 A. M.) | Light blue | 1 |
| 4 (5:26 P. M.) | White turning to red | 1 |
| 5 (2 P. M.) | Yellow turning to red | 1 |
| Total | | 11 |

[1] *Proceed. Cam. Phil. Soc.* **9**, 295, 1898.

were seen soon after sunset and illuminated by the sun, owing to their great height. Seven of these trains can be classed as red, and all the colors observed might be expected in case of illumination by the sun. A number of other daylight trains not given here show the same characteristic colors.

### III. VISIBLE DURATION OF METEOR TRAINS

The time that a meteor train seen at night remains visible depends on the initial intensity of the train, the state of the atmosphere, the altitude of the train above the horizon, the distance between the train and the observer, and also on the keenness of the attention of the observer. Some idea, however, of the average duration can be had from the following reported observations. In a list of meteor trains collected, 53 trains having a duration of more than one minute were as follows:

6 remained visible over 40 (40–60) minutes
7 remained visible over 20 (20–40) minutes
12 remained visible over 10 (10–20) minutes
12 remained visible over 5 ( 5–10) minutes

There were therefore 37 trains which remained visible to the naked eye from five minutes to one hour, the average of 53 trains being 14.8 minutes.

Thus it is seen that many meteor trains persist for ten or twenty minutes after first appearance. In the opinion of the writer, the phenomenon is a gas phosphorescence; first, because of the rapid lateral expansion of the train, evidently a gas diffusion amounting to a mean rate of over 100 meters per minute; second, because of the great volume contained within the boundary of the train, usually being a matter of several cubic miles; and third, since the observed spectrum appears to consist of a few bright lines.

Whatever may be the exact nature of the excitation of the phosphorescent light of meteor trains, the rate of decay of the glow seems likely to correspond to the rates found by laboratory experiment. Nichols and Merritt have established the fact that in the case of phosphorescent solids, such as zinc sulphide, the luminescence decays according to the formula $I=\frac{1}{(a+bt)^2}$, an expression first suggested by Becquerel[1] in 1891.

[1] *Physical Review*, **22**, 279, 1906

Recently the writer has shown by experiments on the afterglow formed in air at low gas pressures by the electrodeless ring discharge, that the rate of decay of luminosity of a phosphorescing gas is expressed by the same law exactly. The curves, shown in Fig. 2, are specimen decay curves of this gas phosphorescence, and the straight lines in Fig. 2 were obtained by plotting $I^{-\frac{1}{2}}$ instead of $I$, $\frac{1}{2}I^{-\frac{1}{2}}$ instead of $\frac{1}{2}I$, etc. From the formula it is possible to compute

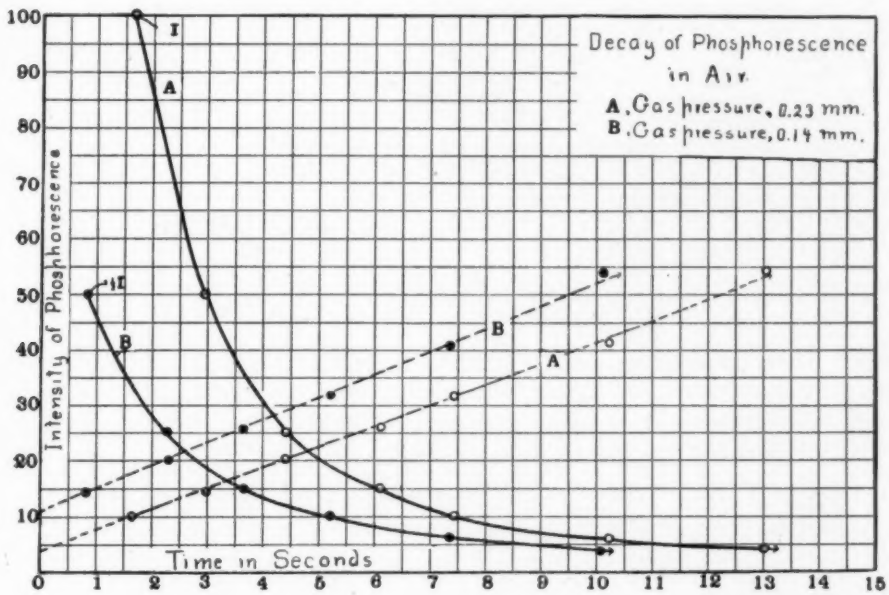



FIG 2 —Curves Showing the Decay of Phosphorescence in Air at Two Different Gas Pressures

the value of intensity of the glow, after it has been fading for 10 or 20 minutes. The value found for the intensity can be considered to be approximate, even if the law does not hold exactly for long-time phosphorescence.

The intensity at the end of 20 minutes is found to be $\frac{1}{250000}I$ ($I$ = standard luminosity used in experiments), a value so small as not to be visible in a discharge tube of 4 centimeters diameter. The limit of visibility of the phosphorescence in a tube of these dimensions seems to be about $\frac{1}{70000}I$. If the meteor train is considered to be a gas phosphorescence of the same nature as the afterglow and is one

mile in thickness, then the total effective luminosity would be of the order of 20,000 times the brightness of the afterglow in the discharge vessel, making no allowance for distance, the intrinsic brightness being about the same intensity, or $\frac{20000}{2500000} I$. This value, about $\frac{1}{12} I$, is equivalent to the intensity of the light which is reflected from a slightly tinted screen of paper placed about 2.35 meters from an electric lamp of 6.5 candle power, an intensity of illumination which would seem to be amply great enough to appear bright in the sky. This calculation is only meant to show that the order of brightness of a phosphorescent gas, even after it faded for twenty minutes, is great enough for visibility provided there is a thick enough layer of radiating matter. If the meteor train is a gas phosphorescence, its long visible duration would appear to be readily explained. Moreover, the rate of decay for the afterglow has been found to be very much slower at lower pressures than the rates in the examples given, and also slower at higher pressures under certain conditions. In fact, on one occasion the gas was visibly phosphorescent, although very faint, 19 minutes after an excitation. The decay curves shown in Fig. 2 were obtained with a special photometer devised for the purpose by the writer. These curves were each formed by one decay of the afterglow only and show the smallness of the experimental error. No work on the decay of gas phosphorescence appears to have been done previous to this.

## IV. EXPLANATION OF THE METEORIC GLOW OR "AURORAL LIGHT"

A curious brightening of the sky has been noted during meteoric showers around the region of the radiant point of the meteors. Professor Challis (Cambridge, Eng.), in reporting his observations on the Leonid shower of November 13, 1866,[1] made the following statement, which is perhaps the best record of the phenomenon:

> During a great part of the time over which the observations extended, there was a kind of glow throughout the heavens, a phenomenon which I was familiar with by my previous experience at the Cambridge observatory, and which my assistants also noticed and were accustomed to call "auroral light." It was however never accompanied by auroral streamers. Mr. Glaisher has informed me that the magnets at Greenwich were remarkably quiet during the night of November 13, 1866.

[1] *Monthly Notices*, **27**, 75, 1867.

The explanation of the phenomenon would appear to be as follows: During the shower mentioned fully 2,000 meteors per hour were recorded as shooting from the radiant of *Leo*, in fact many observers reporting over 100 per minute. While a small percentage of these meteors produced visible trains, each meteor must have produced a train of phosphorescent matter of a certain degree of luminosity; also at any one time all the trains were in different stages of decay of luminosity, but *all* were giving forth some radiation. Several thousand feebly luminous trains were thus diffusing through the atmosphere around the radiant point of the shower. The trains were of course invisible individually, but in the aggregate were probably sufficiently luminous to make a pale light in the region of the sky through which the meteors had passed. If the meteor train is the same as the gaseous afterglow which can be produced in the laboratory, then a phenomenon precisely similar to the described "auroral light" would be expected in every great meteor shower.

## V. PROBABLE EXPLANATION OF THE DUAL APPEARANCE OF TRAINS

Many meteor trains appear double, as if formed by a double nucleus. This explanation of their double appearance was held by H. A. Newton, of Yale University, who, in reporting the observations of Gilman, November 1868, made at the Palisades Observatory, N. Y., states his opinion thus: "I think the double train of this meteor and other meteors is due to the actual duality of the meteor itself." Three drawings of double trains are reproduced in this paper from illustrations accompanying Newton's paper[1] describing the Leonid shower of 1868. This question is of importance, for while it is to be expected that in very rare cases the meteor would break in two, becoming two nuclei, and form a double train, from a study of many other trains by the writer the double appearance of the trains appears to be due rather to a greater luminosity on the border of the train than to a double train formed by two nuclei. The double train is then explained on the hypothesis that the train gradually becomes a tube of luminous matter which, viewed from the side, appears like a double line of

[1] *American Journal of Science and Arts*, **47**, 399, 1869, and Plates.

light. The effect may be caused either by the dying-out of the luminosity along the axis of the train, or a greater luminosity at the border.

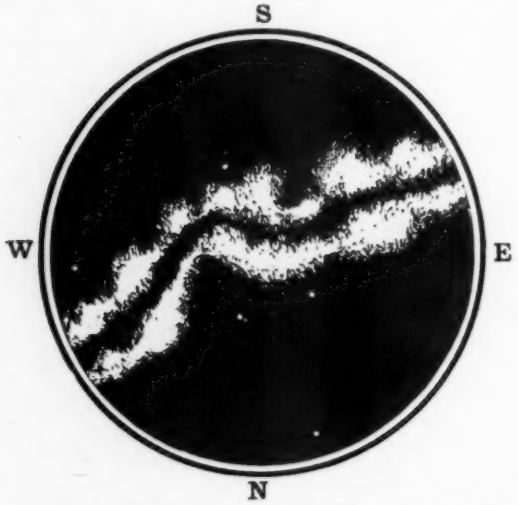



FIG 3.—Train Appearing Double as Seen in the Telescope.

Some of these double trains are shown by

Figs. 3, 4, and 5, which were originally drawn by W. S. Gilman, Jr., of the Palisades Observatory, N. Y., where the trains were observed.

Fig. 3 shows train of a meteor which appeared at 1:53 A. M., Nov. 14, 1868, in a 4-inch telescope, magnifying power 40.

Fig. 4 is another train as seen by telescope which appeared at 2:48 A. M. on the same evening and is referred to by Gilman thus: "The train was double (*as often observed during the evening*) and terminated in an oval cloud at right angles to the direction of the meteor's flight."

Fig. 5 shows a train which appeared at 11:25 P. M. also on the same night, Nov. 3, as seen by the naked eye. "In the telescope, power 40, diameter of field 43′, it presented a double line of bluish-green luminous matter."

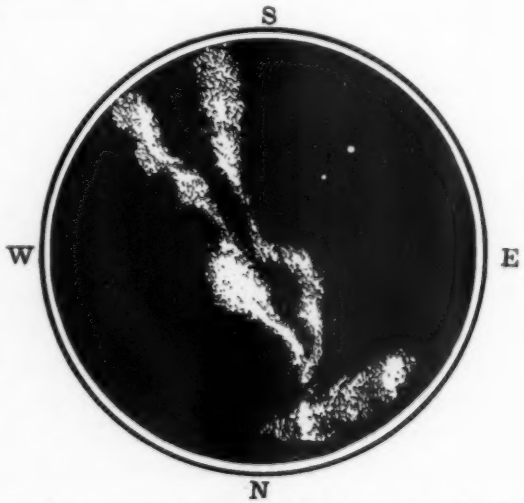



FIG. 4.—Train Appearing Double as Seen in the Telescope.

It is evident from the foregoing that many meteor trains which would appear to the naked eye like a single bar of luminous matter might exhibit a dual appearance if observed through a small telescope.

A number of descriptions of meteor trains seen at night also substantiate the writer's view in regard to the greater luminosity on the border of the train. Thus, No. 53 of the writer's catalogue, November 14, 1868, 2:33 A. M., Madrid, Spain, is described thus: "A large fireball in *Ursa Major* left a train visible ten minutes which expanded 6°–8° in width, then faded out in the center so as to form a ring." Also No. 82, a very wonderful train seen at midnight at Grahamstown, South Africa, October 22, 1895, and carefully reported: "The train was 30° long, and widened out to one degee at one end and three-quarters of a degree at the other. The edges of the train were brighter than the center," etc.; visible 30 minutes. Professor E. E. Barnard observed a train in November 1901, which gradually expanded so as to appear "like a comet with a double tail." A drawing of this train was sent to the writer by the observer, showing the changes in the shape of the train. An observation of a long bright double train was made by W. Shackleton, on October 12, 1904, 11:39 P. M., London.[1] A portion of the report is as follows: "The train was tubular or consisted of two parallel narrow ribbons, each component being about twice the angular diameter of *Jupiter*, or about 90″ in width, separated by an interval of 5″." The train was observed in a telescope and remained visible for nearly twenty minutes. There are other good drawings and records of double night trains not mentioned above. Barnard mentions two trains brightest in the center,[2] as follows:

FIG. 5.—Train as Seen by the Naked Eye, Which Appeared Double in the Telescope.

Train No. 112, August 5, 1882, 9 P. M.: "It appeared at first very bright and unbroken, straight as a shaft, clean and sharp in

[1] *Monthly Notices, R. A. S.*, **66**, 89, 1904.

[2] *Sidereal Messenger*, **10**, 426, 1891.

outline, and brighter along the axis, but in *two seconds*, it became crooked and sinuous, etc." Also train No. 113, August 12, 1882, 3 A. M.: "watched in the telescope for nearly *five seconds*, in which it appeared long and perfectly straight, much brighter along the axis."

These observations tend to confirm rather than to refute the theory of the tube-like distribution of the luminosity of the train, since if the rate of the decay of the phosphorescence is more rapid, directly in the meteor track, the light would be at first bright and then faintest along the axis of the train. The bright axis was observed in the two cases mentioned above apparently only immediately after the train was formed. In all cases of "double trains" described, the

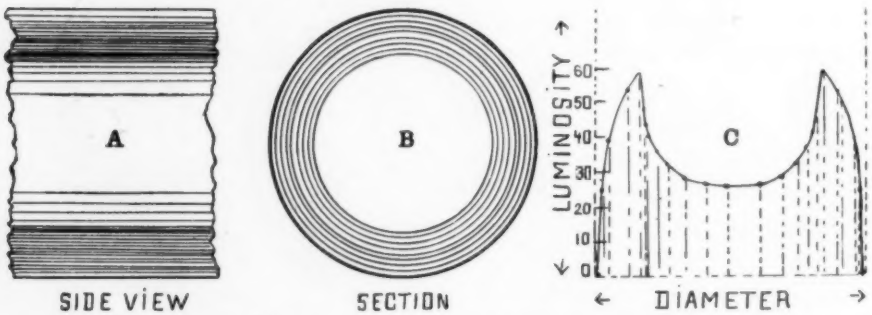



FIG. 6.—Graphical Explanation of the Dual Appearance of Meteor Trains.

observations were made at least one minute after the formation of the trains.

In Fig. 6, *A* shows a side view of a tube of luminosity such as is supposed in the case of a meteor train. *B* shows the tube in cross-section, end on, and *C* gives the variation of luminosity of a tube of luminosity such as *B* as seen from the side. The luminosity near the outside is twice as great as that in the center, although of course the luminosity of the meteor train would not be so uniformly tube-like. If the luminosity was distributed throughout a cylinder, the train as viewed from the side would appear brightest in the center; but as has been shown the reverse appears to be the case. Records indicate that trains obscure stars but little over which they pass, hence the absorption factor cannot be very great. In this connection it is important to note that gaseous glows are brighter with increased

thickness of the glowing volume, as shown in the case of the "afterglow" in the laboratory, and also that observation has been made to the effect that meteor trains observed end on, or those formed by meteors falling directly toward the observer from the radiant, are usually brighter than those seen from the side.[1]

*Double appearance of daylight meteor trains.*—A few trains shining by the reflected light of the sun show double lines of cloud. A meteor train as seen in twilight from Paris, June 11, 1867, 8 P. M., is shown in Figs. 7, *A* and *B*. The drawings are copied from those made by M. L. Roussy, chromometer-maker of the Toulouse Observatory.[2] In Fig. 7, *A*, the train is shown as it appeared 8 minutes after the passage of the meteor; in *B*, as it appeared about one hour later at 9 P. M., and described by the observer as follows: "The point *a*, formed by the apex of the triangle where two lines of the streak *ab*, *ac*, met together without any portion of the streak between them." This observation shows the gradual formation of a double train out of one which was single at first. In this case the train was probably shining in sunlight; hence the double track in this case may have been an increase of cloud density near the outside of the train, not unlikely a condensation phenomenon. Two different drawings by other observers also show duality of the same train.

Two other trains both seen in twilight in eastern United States, August 24, 1869, trains Nos. 55 and 56 of the writer's catalogue, were reported as expanding into double trains, but only the latter appears to be a double train as shown by the observer's drawings. The ring effect which appears in the picture of No. 55 was undoubtedly produced by perspective.

There is thus seen to be not a little data to substantiate the view that the trains gradually become tube-like.

Further facts are required for a definite conclusion in this matter. It is an important feature of the investigation, however, since under some conditions phosphorescent glows in gases appear to decay more rapidly in the immediate region where they are formed. The double train of daylight meteors observed may possibly be due to an acci-

[1] Wood, *Report of British Association for the Advancement of Science*, 1867, p. 83 (L. M. Com.).

[2] *Ibid.*, p. 380.

dental formation, since the only records of double daylight trains yet found by the writer are No. 31, shown in Fig. 7, and No. 56, mentioned above.

## VI. DIFFUSION OF METEOR TRAINS

Almost all descriptions of meteor trains agree that there is a gradual enlargement of the phosphorescent streak. The change is usually referred to as the "expansion of the train." In many cases the extent of this expansion has been noted at several intervals of time after the formation of the train. The phenomenon seemed to be clearly a case of gas diffusion. This is shown by a comparison of numerous records. That the matter is a highly important one needs no argument, because it is evident that if accurate observations are made of this diffusion in the future and the observations made in the past are thoroughly studied, it is likely the pressure of the atmosphere at an altitude of 50 and 60 miles can be determined with approximation. This portion of the study of meteor trains is a long research in itself; therefore no definite conclusion can be arrived at now concerning the pressure of the atmosphere in the meteor train zone. In several cases the dimensions of the trains have been found in the records, and from these the mean rate of diffusion has been determined. These values are given in Table IV together with three trains carefully observed, but where the altitude above the earth has been assumed by the writer to be 60 miles and the rate of diffusion calculated on that basis. In these cases it was necessary to find the distance of the train from the observer by the use of star globe and some simple computations.

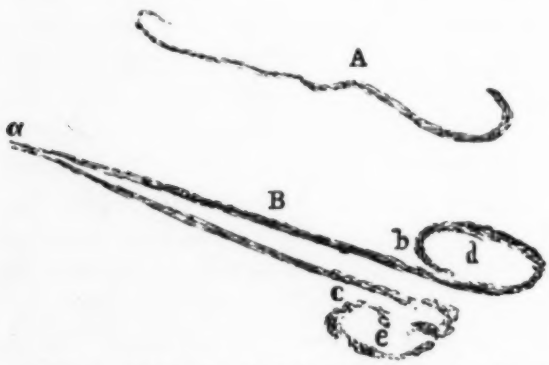



FIG 7.—Train of a Twilight Fireball Showing Cloud Appearing Double.

TABLE IV

DIFFUSION OF METEOR TRAINS

| No. | Width of Train —Miles or Degrees | Time Expanding —Minutes | Mean Velocity, Meters per Minute | Mean Diffusion Rate, Meters per Second | Height of Train—Miles |
|---|---|---|---|---|---|
| 12..... | 1 mile | 10 | 80.5 | 1.3 | 56 |
| 29..... | 3 miles | 9 | 274.0 | 4.5 | 60 |
| 80..... | 4 miles | 17 | 189.0 | 3.1 | 54 |
| 87[1]..... | 1½° | 16 | 95.0 | 1.6 | 60 |
| 90[1]..... | 1° | 10 | 117.2 | 1.96 | 60 |
| 130[1] ..... | 30′ | 6 | 97.8 | 1.63 | 60 |
| Mean values. | | 11.3 | 141.0 | 2.3 | |

[1] Altitude estimated to be 60 miles or 96.6 kilometers. In the other three cases the meteor trains were observed from two or more stations widely apart and the altitudes measured. No. 80 was without any question affected by rapid drift of the atmosphere (125 miles per hour), and hence gives too large a value for diffusion. In all probability the mean diffusion rate of both 29 and 80 is much too high. The numbers in the first column refer to the writer's meteor train catalogue. No. 87 was observed at two stations but the height has not been calculated.

Fig. 8 shows the method of calculating the mean diffusion rate of the train when its diameter is known at a definite time after its formation. This of course gives only the average diffusion. The particular train used in this illustration was No. 87, observed by R. M. Dole of Jamaica Plain, Mass., in 1901, and also shown in *D*, Fig. 9. On the assumption that the altitude of the train was 60 miles (96.6 kilometers) the train was 1.9 miles (or 3.06 kilometers) broad. From this it follows that the gas particles of the train diffused 1530 meters in 16 minutes, or at the average rate of 96.0 meters per minute, or 1.6 meters per second, the diffusion probably being very much greater at first.

The rate of diffusion is supposed to be inversely proportional to the pressure but directly proportional to the square of the absolute temperature, and according to the rates for diffusion at atmospheric pressure and normal temperature for ordinary gases would give a rate at very low pressure and low temperature about the same order as that shown by meteor trains, but nothing more definite can be said at present.

The diffusion of the afterglow formed by the electrodeless discharge is of the same order also, but definite experiments have not been made in that direction. When laboratory experiments are completed along these lines, and accurate meteor observations made,

both of which should not be difficult, the matter will assume a more precise character.

In regard to the observation of meteor trains for diffusion, a good instrument to use would be a small telescope such as a comet finder, for example, 40 magnifying power, with some micrometer device for measuring the width of the train in successive intervals of time after its formation.

The diffusion soon after the formation of the train is desirable, because if there is a high velocity of atmosphere drift at the time, for example, 100 kilometers per hour, the train will be soon distorted by air currents. Also it is important that the diffusion at different parts

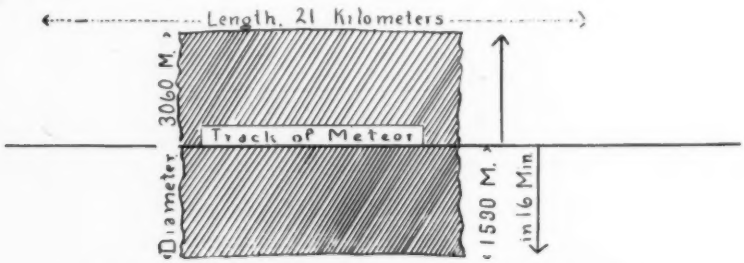



FIG 8.—Showing the Rapid Diffusion Rate of a Meteor Train.

of the train be measured, because it appears probable from the descriptions and drawings of meteor trains that have been made that there is greater diffusion at the upper end of the train than at the lower as indicated by the trains shown in Fig. 9.

This apparent effect may not be real owing to the effect of perspective, for there are many drawings of trains which are quite cylindrical in appearance. It would be well for meteor observers to make special note of this matter in future.

Trains shown in Fig. 9:

A. Train observed at Sunderland, England, by T. W. Backhouse, November 14, 1866, 2:21 A. M. (*British Association for the Advancement of Science Reports*, 1867, p. 37.)

B. Train observed over the Persian Gulf, June 9, 1883, 7:51 P. M., by H. Harrison. (*The Observatory*, **6**, 271, 1883.)

C. Train observed at Sunderland, England, by T. W. Backhouse, November 14, 1866, 2:41 A. M. (*British Association for the Advancement of Science Reports*, 1867, p. 377.)

D. Train observed at Jamaica Plain, Mass., by R. M. Dole, November 15, 1901, 5:09 A. M. (*Popular Astronomy*, **10**, 53, 1902.)

E. Train observed at Sunderland, England, by T. W. Backhouse, November 13, 1888, 5:19 A. M. (*Monthly Notices*, **49**, 66, 1888.)

$F_1$. Daylight train, eastern United States, observed by J. S. Helles, August 24, 1869, after sunset. (*British Association for the Advancement of Science Reports*, 1870, p. 89.)

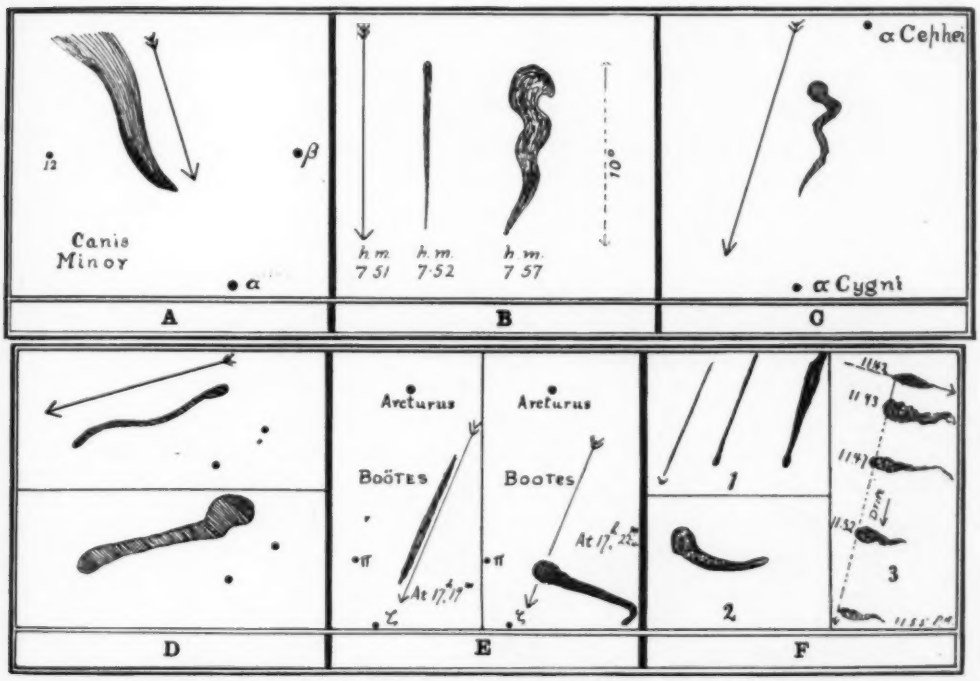



FIG 9.—Trains Which Indicate a Greater Diffusion Rate With Increase of Altitude.

$F_2$. A train seen at Wishbeach, England, by S. H. Miller, Nov. 14, 1866, 3:07 A. M. (*British Association for the Advancement of Science Reports*, 1867, p. 319.)

$F_3$. Train observed at Bristol, October 13, 1900, 11:42 P. M., by W. F. Denning. (In letter to writer and not previously published.)

## VII. THE DRIFT OF THE ATMOSPHERE AT GREAT ALTITUDES

In making a search for facts relating to meteor train phenomena, in the case of more than sixty trains it was found that the drift of the train over the surface of the earth had been observed. The

directions have all been reduced to points of compass, and the summary shows that, of the daylight meteors, seven out of nine trains illuminated by the sun drifted toward the west. These were probably at a lower altitude than 50 miles. Fifty-three trains observed at night, and probably at an altitude below 45 and 65 miles, drifted in various directions as follows: North 10, northwest 4, east 12, southeast 12, south 6, southwest 4, west 0, northwest 2; and in two different directions in different strata, 3. The facts appear to confirm Barnard's view that there is an easterly current over the North Temperate zone, for the currents predominate in that direction, but it was found that many trains drifted north and south and even to the northwest and southwest.

The facts also indicate that there are often zones of calm of perhaps 5 to 10 miles in depth, while directly above and below may be swift air currents, and that there are usually several zones with currents in opposite directions in the region above 30 miles altitude. The observations in England and Scotland show that 15 in 21 trains drifted toward the southeast quarter of the compass (E., SE., or S.), while in the United States 21 in 32 trains drifted toward the northeast quarter (E., NE., and N.), indicating a probable difference in the predominating upper drifts corresponding to different latitudes. A paper giving the facts of the train drifts in detail will appear in the *Monthly Weather Review*.

## VIII. RESEMBLANCE OF THE METEOR TRAIN TO THE AFTERGLOW PRODUCED BY THE ELECTRODELESS RING DISCHARGE

The self-luminous train resembles the afterglow produced in a gas by the electrodeless discharge in the following points:

1. The meteor train as well as the afterglow appears to be produced between definite low gas pressures; in the former case the atmospheric pressures corresponding to the altitudes between 50 and 60 miles, in the latter the air pressure in the discharge tube between 0.5 and 0.05 mm.

2. The rate of diffusion of the afterglow at certain pressures is of the same order as the outward diffusion of the glowing particles of the meteor train, or at about the rate of a hundred meters per minute.

3. The visible spectrum of both the afterglow and the meteor

train is chiefly composed of a few lines or narrow bands. The spectra of meteor trains observed by Herschel and von Konkoly are recorded as consisting of a yellow line and a green line, attributed to sodium and magnesium respectively, but the identification was not quanittatively determined.

4. Under certain conditions the afterglow appears to die out first where it is formed, and observations have shown that many meteor trains are tube-like, and it is possible that they may fade first in the center, or directly in the meteor's track where the train originates.

5. The afterglow can occur in air cooled to $-186°$ C. The glow from the meteor train proceeds from a mixture of gas and extremely fine meteoric dust at the very low night temperature which exists at 50 or 60 miles above the earth's surface.

6. The afterglow is supposed to be produced by a polymerised gas gradually returning to its former condition accompanied by radiation.

The motion of the meteor through the atmosphere produces a temperature of many thousands of degrees centigrade, and may bring about chemical or physical changes in the composition of the atmosphere which on gradually reverting to its original state gives out a phosphorescent glow. It is not unlikely that the phosphorescence is connected directly with the highly ionized state of the air produced by the very high temperature of the nucleus, the effects being intensified by static electrical conditions, which are probably of considerable magnitude, produced by the rush of the meteor through the air with a velocity of from 20 to 30 miles per second.

## IX. SUMMARY OF THE CHIEF RESULTS OBTAINED

A summary of some of the results of the investigations concerning meteor trains is as follows:

1. The meteor trains are self-luminous gas clouds combined with very minute meteoric dust particles, the latter in daylight reflecting light like ordinary clouds.

2. The height of meteor trains seen at night appears to be at a definite altitude, indicating that the phosphorescence is dependent on the gas pressure where the trains are formed.

3. The diffusion of the train is gas diffusion and its rate depends

on the pressure and temperature of the atmosphere, and probably on the initial intensity of the train.

4. Many meteor trains appear to be tubular in form, that is, the luminosity is greatest near the border.

5. Experiments have been made by the writer which give the law for the rate of decay of the phosphorescence of air at very low pressures, and these experiments explain the long visible duration of the meteor train, on the hypothesis that it is a phosphorescence which decays according to the same law.

6. Statistics on the color of trains show that, excluding those illuminated by sunlight, trains are as a rule green or yellow fading to white, colors which are typical of the phosphorescence of air.

While it is not at all certain that the light of the meteor trains is a gas phosphorescence that is identical with the afterglow which follows the electrodeless ring discharge, yet the phenomena are similar in many respects. It is hoped that precise spectroscopic observations can be obtained of a meteor train and the positions of the yellow and green lines observed by Herschel and von Konkoly exactly determined. The latter observed the green line to last for over ten minutes in the case of one train. The photographic spectrum of the meteor nucleus should contain the bright lines of the train combined with a continuous spectrum and bright lines from the incandescent nucleus, but it is likely that the train spectrum would be relatively feeble.

I desire to express my thanks to the members of the Astronomical Staff at Columbia University who have placed the facilities of their department at my disposal and have kindly assisted me on various occasions.

PHOENIX PHYSICAL LABORATORY
COLUMBIA UNIVERSITY
June 1907

# ON THE DOPPLER EFFECT IN THE SPECTRUM OF HYDROGEN AND OF MERCURY

## COMMENTS ON MR. STARK'S ARTICLE

By G. F. HULL

Paschen's confirmation of Stark's result regarding the existence of the Doppler effect for the mercury lines makes it clear that under certain conditions some of the luminous particles of mercury in the canal stream of that gas are in rapid motion. In some preliminary measurements made eighteen months ago I found a shift of the mercury lines from the canal stream. The result was announced in the *Proceedings of the Royal Society* of June 1906. But a large number of plates taken later showed no shift. In these later experiments higher potentials were used and greater care was exercised to eliminate errors due to temperature changes and vibrations. Moreover, I failed to observe a Doppler effect for helium (except a very small one); so I was led to the conclusion that my first results in the case of mercury were accidental, and that in general the luminous mercury particles in the canal stream were not in motion.

To account for these negative effects in mercury and helium I advanced the hypothesis that the stream of positively electrified particles, when mercury or helium filled the tube, was not composed of the particles of either of those gases, but was probably composed of hydrogen, the particles of which are easily positively electrified and set in rapid motion. That hypothesis has been confirmed, not only by experiments which I have conducted during the past winter but also and chiefly by the investigations made by J. J. Thomson and published in the *Philosophical Magazine* for May 1907. Professor Thomson found that

> whatever kind of gas be used to fill the tube, or whatever the nature of the electrode, the deflected phosphorescence (caused by the canal stream) splits up into two patches. For one of these patches the maximum value of $\frac{e}{m}$ is about $10^4$, the value for the hydrogen atom; while the value for the other patch is about $5 \times 10^3$ the value for the $\alpha$ particle or the hydrogen molecule. . . . . The interest of the experiments at very low pressures lies in the fact that in this case the rays

are the same whatever gas may be used to fill the tube; the characteristic rays of the gas disappear, and we get the same kind of carriers for all substances (p. 573).

In the case of helium under certain conditions, Professor Thomson found that there was a third particle acting as carrier, viz., a particle of the size of the helium atom. But helium was the only gas among oxygen, nitrogen, carbonic oxide, hydrogen, helium, neon, showing a characteristic ray, and even helium ceased to be an exception when the discharge potential was high. Professor Thomson does not state that he tried mercury vapor but I infer from his article that he would expect to find a motion of the mercury atoms, if at all, only at small discharge potentials.

It seems clear from these experiments that the particles of the gas (excepting hydrogen) filling the tube need not be, and at higher potentials probably are not, the carriers of the current. That was my inference based upon my observations on the canal streams of hydrogen, mercury, and helium.

We are thus confronted with conflicting testimony. From Professor Thomson's experiments we should not expect a Doppler effect in the positive rays of nitrogen. But Stark and Hermann have announced that they have found such an effect. In the case of helium I found that, for the conditions under which I worked, the Doppler effect, if it existed at all, was very small. Confirming this, Professor Thomson shows that a condition exists where the helium particles do not move. But there are other conditions where the helium particles move rapidly, and consequently for these conditions a large Doppler effect should be found. Apparently Dr. Rau[1] has been for-

[1] The only statement published so far by Dr. Rau regarding the Doppler effect in the canal stream of helium is as follows: "Mit der eben angeführten Hypothese stimmt überein dass die Heliumkanalstrahlen nach meinen Beobachtungen den von Herrn Stark entdeckten Dopplereffekt nicht oder doch nicht in der zu erwartenden Grösse zeigen. Ich konnte ihn unter Benutzung eines Kirchhoffschen Spektralapparates mit vier Prismen trotz der grossen Helligkeit des Spektrums weder bei subjektiver Beobachtung noch auf Photographien (bis 15 Stunden Beleuchtungszeit) wahrnehmen; eine nähere Untersuchung musste natürlich mit dem Gitter erfolgen." —*Physik. Zeit.*, 7, 423, 1906.

The optical system used by Dr. Rau was sufficient to have shown the Doppler effect expected in the case of helium had it existed, viz., a few Ångström units. The potentials he used were high enough. The conclusion is therefore that very few luminous helium particles were carriers of the positive charges.

tunate in working with these conditions. In the case of mercury vapor I found no certain Doppler effect. Professor Thomson's experiments lead us to expect no effect for high discharge potential. But Professor Stark claims that the effect is found only when the potentials are high. It is obvious that our experimental evidence is not complete in regard to the conditions under which the Doppler effect may be present or absent.

There are other points in which my results do not agree with those obtained by Professor Stark. I found no polarization of the light from the canal stream, while Professor Stark claims that a polarization exists. I found no shift of the lines of the canal spectrum of hydrogen, viewed at right angles to the direction of the stream, in comparison with the lines from a Plücker-tube spectrum. Professor Stark found that the canal-spectrum lines of hydrogen, so viewed, are displaced toward the red when compared with the slow-moving lines of the negative glow. The displacement seems to be proportional to the wave-length and also to the square of the velocity. The displacement of the center of $H\beta$ is approximately 0.8 Ångström units for a velocity of $1.2 \times 10^8$ cm. sec.$^{-1}$.

Obviously in view of so many discordant results one should be slow to construct elaborate theories in regard to the canal rays. I feel like quoting in this connection a statement made by Lord Rayleigh in a recent number of the *Philosophical Magazine:* "There is much in the behavior of vacuum tubes which at present defies explanation."

In conclusion I wish to note that, if the spectrum of the mercury lines from the canal stream consists of a strong stationary line accompanied by a broad, faint, displaced component, the echelon-prism which I used would not be a satisfactory analyzer of the radiation. For the faint component would appear as a very broad hazy line, near the center of which would be the strong line. This was a result for which I was constantly on the lookout, but which I did not detect. Nor did I find a faint displaced component on the few test plates taken with a 60° prism.

DARTMOUTH COLLEGE
June 26, 1907

# NOTE ON DISPLACEMENT OF SPECTRAL LINES

By J. LARMOR

The important paper by Mr. Humphreys (this Journal, **26**, 18, July 1907) gives data for somewhat closer scrutiny of the origin of the pressure-shift of lines in the spectrum. The change must be connected with electric properties of the surrounding gas; mechanical pressure arises merely from the translatory motions of the molecules, and these are so slow as hardly to count in connection with radiation-periods. Thus the phenomenon is probably more strictly describable as a density-effect. Electrically, the effect of increase of density is to increase the inductive capacity of the medium, that is, to diminish the effective aethereal elasticity which propagates the radiation. This is the averaged result; each molecule individually, through the agency of its plastic field of force or aether-strain, provides a yielding region in the aether in which the effective stiffness is diminished. The elastic energy which maintains the free vibrations of a radiator is located in its field of force in the adjacent aether; and by dynamical principles any loosening of the constraint in that field such as an adjacent molecule would produce, which would itself be somewhat intensified by equality of period, must in general tend toward increasing the free period, involving displacement of the radiation toward longer wave-length.

By known dynamical principles[1] the change in free period due to slight change of constitution of the vibrating system can be estimated, by calculating the altered kinetic and potential energies of the type of vibration under consideration on the assumption that the type remains unaltered.

In the present case some light may be thrown on the amount of effect to be expected, by supposing the vibrating molecule to be situated in the center of a sphere of free aether, beyond which the molecularly constituted gas is taken to be smoothed out into a uniform medium having the inductive capacity $K$ of the gas. The type of vibration being retained as before, its kinetic (magnetic) energy is not thereby

[1] On this subject see Lord Rayleigh's *Theory of Sound*, §88.

affected from what it would be in a vacuum, but its elastic (electric) energy is altered in the ratio $K^{-1}$, wherever $K$ is different from unity. To obtain a rough estimate, suppose the vibrating aether-field to be that outside a concentric spherical surface of radius $a$, and suppose the electric field to fall off with distance according to the law $r^{-n}$, multiplied of course by a function of direction. The static energy in it, measured from outside up to a concentric spherical surface of radius $c$, will be proportional to

$$\int_c^\infty r^{-2n}\ 4\pi r^2 .\ dr,\ \text{or}\ \frac{4\pi}{2n-3}\, c^{-2n+3}.$$

If therefore the region beyond a distance $c$, equal say to $ka$, is filled with material of inductive capacity $K$, not much different from unity, the total static energy of the vibration is thus altered in the ratio of

$$a^{-2n+3} - c^{-2n+3}(1-K^{-1}) \text{ to } a^{-2n+3},$$

that is, of $1-k^{-2n+3}(1-k^{-1})$ to 1. The frequency of the vibration is increased as the square root of this. For air at pressure of one atmosphere $K=1.0006$, and Mr. Humphreys gives (p. 31) the proportionate change of wave-length as about $10^{-6}$. Thus $k^{-2n+3}\times 0.0006$ is about equal to $10^{-6}$. If the vibrator operates as a simple Hertzian doublet, $n=3$; the other term, which constitutes the radiation, not being of account close to the vibrator. This would make $k^{-3}$ of the order of $\frac{1}{600}$, so that $k$ would be about $8\frac{1}{2}$. In a gas at pressure of one atmosphere the molecules are spaced at a mean distance of very roughly 10 times the molecular diameter; and if $n=3$, only about $\frac{1}{217}$ of the energy of one of them is beyond three molecular radii from its center. Thus it is not unreasonable to replace the influence of the discrete distribution of gas-molecules by that of a uniform averaged medium extending inward to about eight molecular radii from the center of the vibrator. But these *data* are of course far too vague to justify more than the mere statement that the dielectric influence of the neighboring molecules is a *vera causa* of the right order of magnitude. For the next higher type of possible vibration, $n=4$, the value of $k$ would be about $3\frac{1}{2}$, which may be just barely permissible; but for $n=5$, the value of $k$ would be slightly over 2, which would be ruled out. There is thus some presumption that the free vibration corresponding to each line of the spectrum is (except

of course close up to the nucleus) of the simple type of that of a Hertzian doublet source. Moreover if $n$ were not 3, the effect would not be proportional to the density of the gas. We have been estimating the average effect, on which a general broadening of the band due to irregular nearer approaches of molecules is superposed.

The shift has not been observed in band spectra. The vibrator would then presumably be a molecule; and it may not be fanciful to suppose that this circumstance may point to its field of energy being more concentrated into the region between its atoms; a higher value of $n$ would make the difference.

The remarkable one-sided broadening of absorption bands of pure mercury vapor, and its abolition by the admixture of a foreign gas, reported by Professor Wood (this Journal, **26**, 41, July 1907) may perhaps have suggested similar considerations. The tendency to condensation in the pure vapor may proceed to an equilibrium, when the formation of loose molecular aggregates by what may be called adhesion would be balanced by their destruction by collisions. The molecules in such loose aggregates would, owing to their (slight) mutual influence, vibrate in longer periods, and give rise to the displaced part of the band: but the average amount of this incipient aggregation would be much diminished by the admixture of a neutral gas.

CAMBRIDGE, ENGLAND
August 8, 1907

# THE VARIABILITY IN LIGHT OF *MIRA CETI* AND THE TEMPERATURE OF SUN-SPOTS

By A. L. CORTIE

The existence of a banded spectrum in that of sun-spots was first detected in the green region of the spectrum by Secchi in 1869,[1] and in the red by Professor Young in 1872.[2] In the years 1880–1883 many observations of similar bands in the green were made by Mr. Maunder at Greenwich.[3] The bands in the red first seen by Professor Young were independently observed as flutings and their positions ascertained by the Stonyhurst observers in 1885–1886.[4] Flutings are characteristic of the spectra of chemical compounds. Professor Young was led to the conclusion, adopted also by the Stonyhurst observers, that the banded spectrum in sun-spots "would seem to point to such a reduction of temperature over the spot-nucleus as permits the formation of gaseous compounds by elements elsewhere dissociated."[5] Whether the compounds are gaseous or not is beside the question at present discussed, the point insisted upon being that according to this view sun-spots are at a lower temperature than the neighboring photosphere. The recent more elaborate and more precise work carried on both in laboratory and observatory by Professor Hale with Mr. Adams and Mr. Gale at Mount Wilson, California,[6] and by Professor Fowler at South Kensington[7] has served to strengthen the probability of this view. The bands especially observed at Stonyhurst in 1885–1886, were not seen in the spots observed from the autumn of 1886 to that of 1890.[8] It is possible that such bands are a characteristic of sun-spots at the periods near and at maximum spot-activity. They have been recorded, however, in all recent obser-

[1] *Le Soleil*, 2d ed., Vol. I., p. 288.

[2] *Nature*, **7**, 107, 1872.

[3] *Greenwich Photographic and Spectroscopic Results.*

[4] *Monthly Notices*, **47**, 19, November 1886.

[5] *Nature, loc. cit.*

[6] *Astrophysical Journal*, **24**, 185, October 1906.

[7] *Transactions of the Solar Research Union*, Vol. I, pp. 201–229.

[8] *Monthly Notices*, **51**, 76, 1890.

vations by Mitchell at Princeton, Fowler at South Kensington, and at Stonyhurst, and are a marked feature in the superb map of the spectrum of sun-spots recently distributed to observers by the generosity of Professor Hale and Mr. Ellerman. Perhaps only the bands at the red end of the spectrum disappear at the approach of minimum sun-spot activity; a point which needs investigation.

With regard to the origin of the bands seen in the spectrum of sun-spots, Professor Hale and Mr. Adams have identified bands in the deep red, with heads at λ 7054.6, 7088.0, 7125.9, as due to titanium oxide,[1] while more recently Professor Fowler has traced a series of bands in the green as due to magnesium hydride.[2] The existence of spectra of chemical compounds as giving rise to the phenomena of bands in the spectrum of sun-spots is now indubitable. The main purport of the present paper is to show that if we argue from the differences in the spectra of the stars which are generally assigned to temperature as their cause; and especially if the argument be founded on such stars as contain the same chemical compound as has been found to exist in sun-spots, that such a line of argument will tend to strengthen the presumption as to the relatively lower temperature of sun-spots, when compared with that of the photosphere.

The spectrum of stars of Secchi's Type III is characterized by a series of dark bands. These bands were numbered and measured by Dunér, and are known by his name. Stars of this type which show the characteristic bands are *α Herculis*, *α Orionis*, and the variable star *Omicron* or *Mira Ceti*. The bands in *α Herculis* and *ο Ceti* were shown to be due to a compound of titanium by Professor Fowler.[3] This compound of titanium was subsequently proved to be titanium oxide by the same observer. The spectrum of titanium oxide has also been recently recognized in the spectrum of *α Orionis* by Mr. Newall and Mr. Cookson,[4] with the heads of three flutings practically coincident in wave-lengths with those given by Hale and Adams as present in the banded spectrum of sun-spots at λ 7054.6, 7088.0, 7125.9. Hence a connecting link is furnished between the banded

[1] *Astrophysical Journal*, **25**, 77, 1907.

[2] *The Observatory*, **30**, 272, July 1907,

[3] *Proc. R. S.*, **73**, 219, 1904.

[4] *Monthly Notices*, **67**, 482, 1907.

spectrum of stars of Type III and that of sun-spots; and such changes observed in the banded spectrum of the stars of this type as are presumably due to changes of temperature, may serve to throw light upon the question of the temperature of sun-spots. A very complete account of the spectrum of *Mira Ceti* as observed at Stonyhurst at its maximum of 1897 was given by Father Sidgreaves,[1] accompanied by tables of wave-lengths of the bright and dark lines, and of the dark bands. The greatest brilliancy of the star at this maximum was about 3.0 magnitude.[2] At the recent maximum of December 1906, the star attained its greatest luster on the 11th, and reached the higher value of 2.0 magnitude;[3] that is, it was two and a half times as bright and one and a quarter times as hot in 1906 as it was in 1897. A comparison of the two series of plates of the spectrum of the star, secured by Father Sidgreaves at the two maxima, under precisely identical conditions as to the instruments and plates employed, shows a striking change in the relative intensities of the bands. Fourteen bands were mapped between $H\gamma$ and $H\beta$ in the spectrum of 1897, with sharp heads toward the violet, and wings of gradually diminishing intensity toward the red. The positions of the heads of these bands were:

| No. | λ | No. | λ |
|---|---|---|---|
| 1 | 4352 | 8 | 4623 |
| 2 | 4395 | 9 | 4667 |
| 3 | 4420 | 10 | 4713 |
| 4 | 4458 | 11 | 4735 |
| 5 | 4502 | 12 | 4757 |
| 6 | 4544 | 13 | 4803 |
| 7 | 4581 | 14 | 4842 |

In the spectrograms of 1906, the bands numbered 3, 4, 7, 8, 9, 10, 11 are much weaker than in 1897, while those numbered 1, 2, 5, 6 are very much reduced in intensity; in fact numbers 1 and 2 are hardly visible. Yet the character of the bands named remained the same. In the case, however, of bands 12, 13, 14, the winged extensions have altogether disappeared in 1906, leaving strong lines, the

[1] *Ibid.*, **58**, 344, 1898.

[2] *Journal B. A. A.*, **8**, 283, 1900.

[3] *Ibid.*, **17**, 346, 1907.

heads of the original bands, at the wave-lengths named. A brighter maximum in the visibility of the star would presumably indicate that the star is hotter, as well as more luminous, and it is a significant fact, as bearing on the temperature of sun-spots from the bands observed in such spectra, that the difference of about a full magnitude in the light of the star between the maxima of 1897 and 1906 should have resulted in a corresponding decrease in the intensity of the titanium-oxide absorption bands, which compound also gives rise to a banded spectrum in sun-spots.

The $H\beta$ line, which was almost if not entirely extinguished by the possible overlapping of the band $\lambda$ 4842–4884 in 1897, was prominently visible in 1906, while the other lines in the series from $H\beta$ to $H\sigma$, with the exception of $H\epsilon$, covered by the calcium absorption, were easily identified on the plates. The lines $H\gamma$ and $H\delta$ were also winged, presenting an appearance somewhat like that, though on a greatly reduced scale, seen in the hydrogen lines at the outburst of the stars *Nova Aurigae* and *Nova Persei*, as investigated at Stonyhurst. This character of the hydrogen lines $H\gamma$ and $H\delta$, not seen in 1897, also accentuates the much greater luminosity, and concomitant rise in temperature of the star at the last maximum.

Again, the gradual transition of the banded spectrum of *o Ceti* to the line spectrum of Type II, or solar stars, through such connecting links as *α Herculis*, *β Pegasi*, *η Geminorum*, *α Orionis*, *β Andromedae*, and *α Tauri* was demonstrated in 1897 by Father Sidgreaves,[1] who also showed that it was more remote from the solar spectrum than the typical star of Type III, *α Herculis*. The gradual deepening in intensity of the bands as the series passes from *α Tauri* to *o Ceti* would point to a gradual lowering of temperature, when considered together with the greater darkness of the bands of *o Ceti* at a less maximum of brightness. This view coincides with the classification adopted by Sir Norman Lockyer, in which the Aldebarian stars are a step higher on the ascending scale of temperature than the Antarian or stars of Type III.

In a recent paper on the "Spectrum of *Mira Ceti*,"[2] Mr. J. S. Plaskett writes:

[1] *Monthly Notices, loc. cit.*

[2] *Journal of the R. A. S. of Canada*, 1, 56, 1907.

> The only absorbing elements present in the strong and best defined lines, . . . . are *Ti, V, Fe, Mn, Cr.* . . . . the first specified are those which are most strongly affected in the spectra of sun-spots, and which, as Professor Hale and Mr. Adams have shown, are much intensified in the spectrum of *Arcturus*, and still more so in α *Orionis*, as compared with their intensity in the sun. Apparently they are even more prominent in ο *Ceti* than in α *Orionis*. . . . .

Here again is a further link of similarity between the spectrum of sun-spots and that of ο *Ceti*.

Hence, to sum up, the undoubted presence of the chief constituents of the line spectrum of sun-spots as intensified in stars of Type III; the presence of the bands of titanium oxide, also recognized in sun-spots; the partial disappearance of some of these bands, and the total disappearance of others at the greater luminous maximum of *Mira Ceti* in 1906; and this, too, accompanied by a behavior in the hydrogen lines akin to that observed in new stars; the substitution of a line for a banded spectrum in a series of stars on an ascending scale of temperature; these are all facts which, when linked together, point to the conclusion that the temperature of sun-spots is lower than that of the solar photosphere.

STONYHURST COLLEGE OBSERVATORY
July 1907

# *Minor Contributions and Notes*

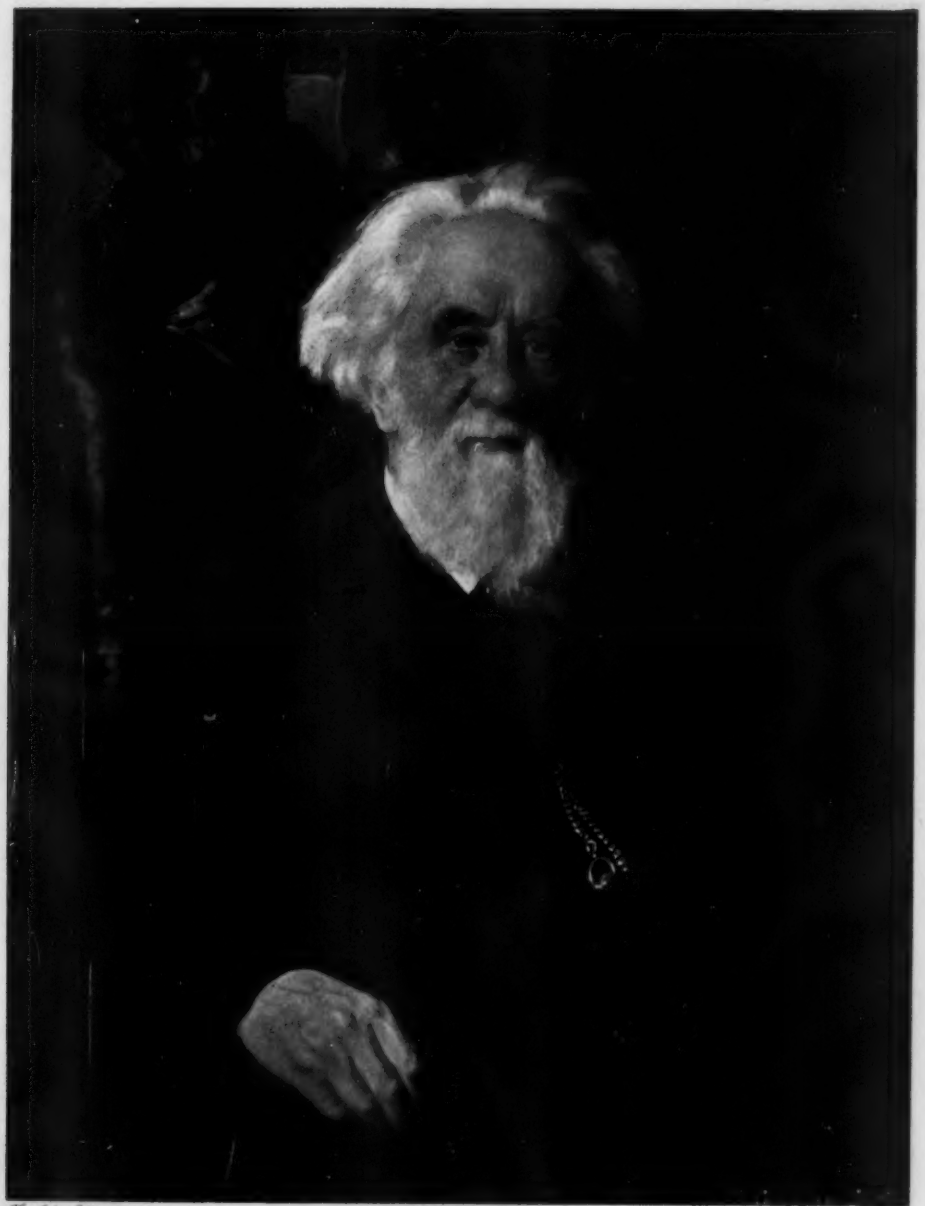
## PORTRAIT OF SIR WILLIAM HUGGINS

The portrait of Sir William Huggins which adorns this number of the Journal is reproduced in photogravure from the painting by Hon. John Collier presented to the Royal Society by certain subscribers on November 30, 1905, at the completion of Sir William's tenure of office as president (1900–1905). The sittings were made at the rooms, and in the presidential chair, of the Royal Society, when the distinguished subject was eighty-one years old. Excepting the immortal Newton, only two others have held this office at so great an age.

The continued activity of many of its pioneers has been one of the compensations for the youth of the science of astrophysics: may this fortunate condition long endure!

We do not here enter upon any discussion of the scientific achievements of Sir William and his gifted collaborator, Lady Huggins, for are they not written in the *Philosophical Transactions* and *Proceedings* of the Royal Society, in the *Monthly Notices* of the Royal Astronomical Society, in the noble volume of *Publications* of the Tulse Hill Observatory, and in the pages of this Journal, as well as in numerous public addresses?

The thanks of the editors are due to the artist and to the committee of subscribers for permission to publish a reproduction of this splendid portrait.



Hon. John Collier, pinxit

SIR WILLIAM HUGGINS

K.C.B. F.R.S.

## BAND SPECTRUM OF VANADIUM

At the end of their most interesting paper on sun-spot spectra[1] Messrs. G. E. Hale and W. S. Adams make the following remark on the band spectrum of vanadium: "Hitherto we have not been able to produce a vanadium band spectrum in the laboratory." Using vanadium chlorate I have never found any difficulty in getting a band spectrum in the arc and even in the spark (with self-induction), that seems to belong to the metal or to the oxide. Professor Hagenbach and I have given a short notice on this band spectrum on p. 37 of our *Atlas of Emission Spectra*, Jena and London, 1905, together with a reproduction of a plate taken with a grating of 1-meter radius; unfortunately all the details of the originals are lost, even in the heliogravures, and only three heads are to be seen in the green and yellow parts of the spectrum.

Two remarks are to be added: first, that there is still some uncertainty about the substance to which the band spectrum belongs; second, that I only wish to facilitate further and more accurate study of the vanadium spectrum by this note, without any claim of priority, although I have not found an allusion to the band spectrum in the papers of Rowland and Harrison, Hasselberg, Lockyer, Exner and Haschek, and Lohse on the arc spectrum of vanadium.

H. KONEN

UNIVERSITY MÜNSTER I W.

June 17, 1907

[1] "Second Paper on the Cause of the Characteristic Phenomena of Sun-Spot Spectra," *Astrophysical Journal*, **25**, 75–95, 1907.

The melancholy announcement has just reached us of the death, on August 13, of Hermann Carl Vogel, the eminent director of the Royal Astrophysical Observatory at Potsdam. Although the condition of his health has given concern to his friends for some years, this fatal termination of his malady, at the comparatively early age of 65, comes as a shock to us who had hoped that he might yet enjoy many years of fruitful activity in the important position which he had filled for a quarter of a century.

A sketch of the life and work of Professor Vogel will appear in an early number of this Journal, of which he had been an associate editor, or collaborator, since its foundation.